Lesson 2
Diffractometers & Phase Identification

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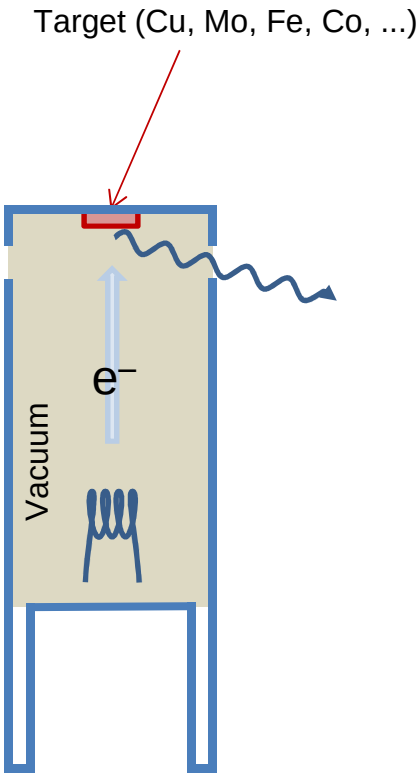
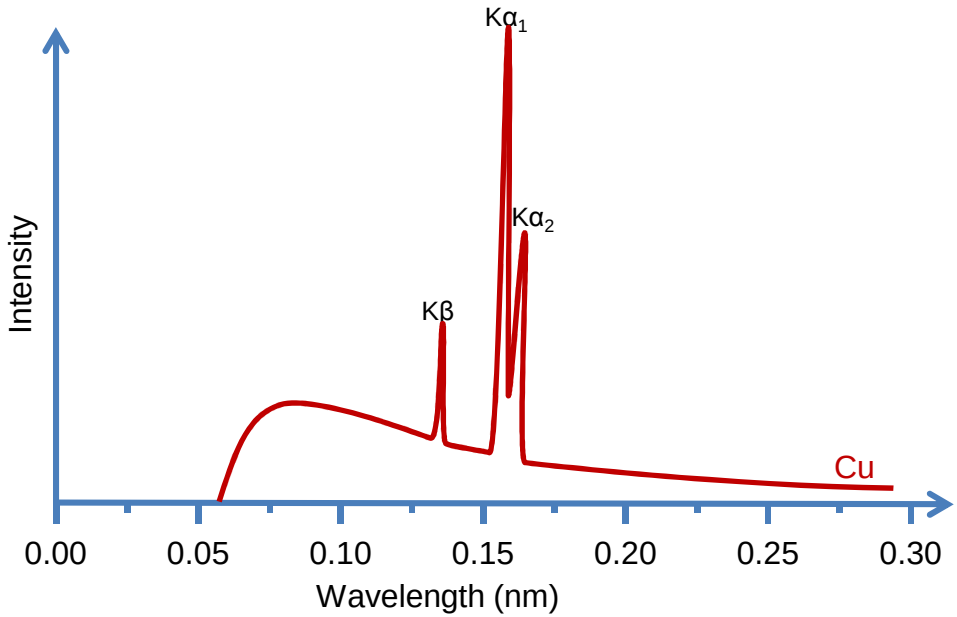
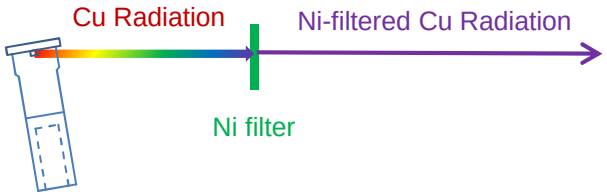
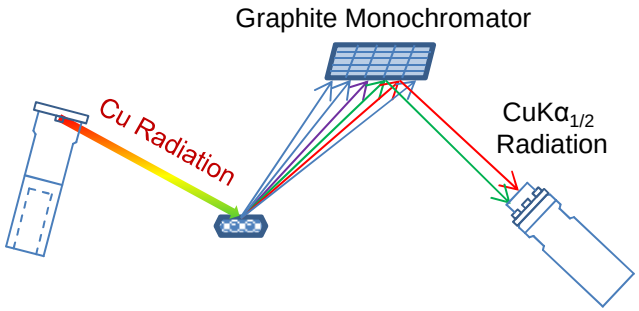
Repetition: Generation of X-rays



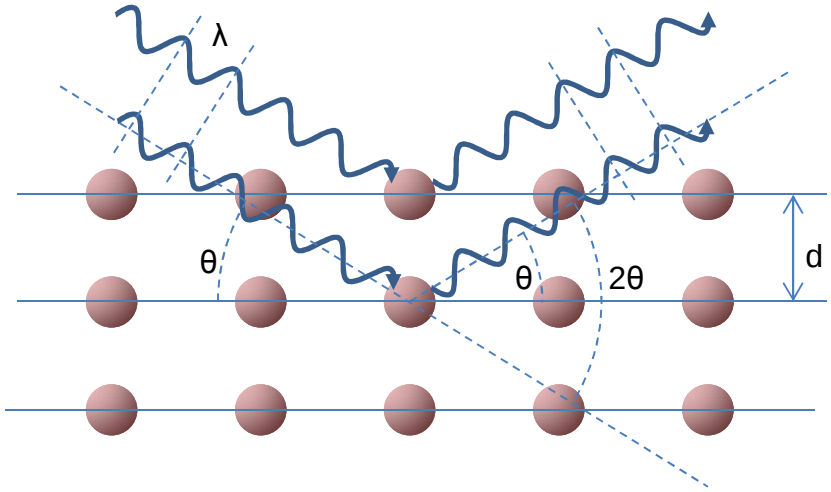


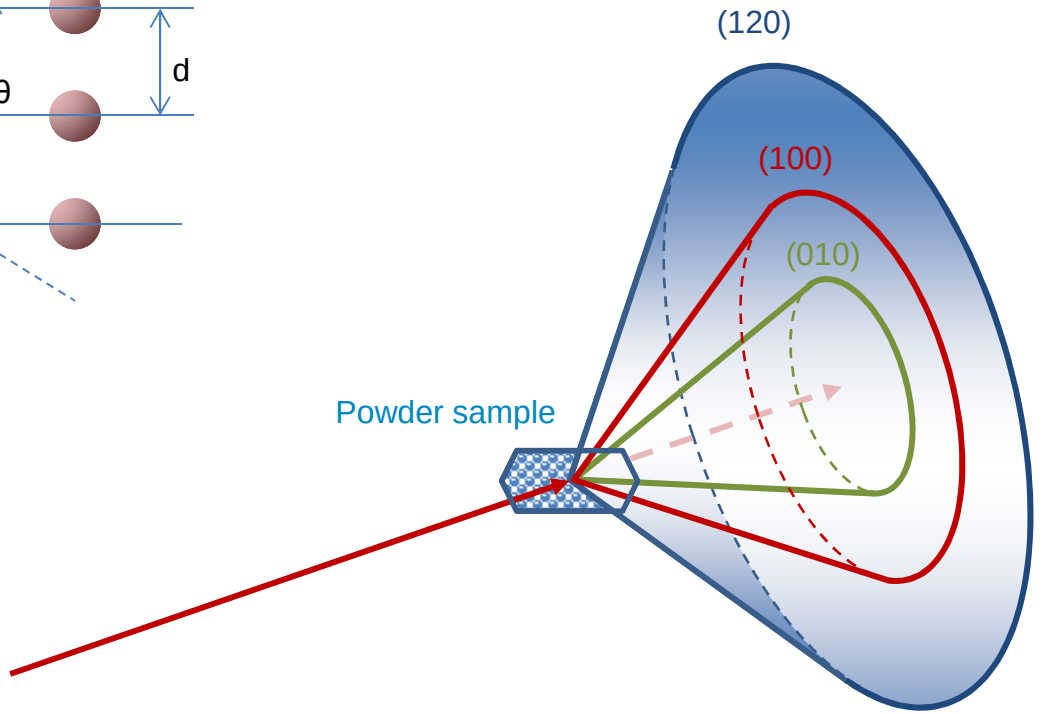




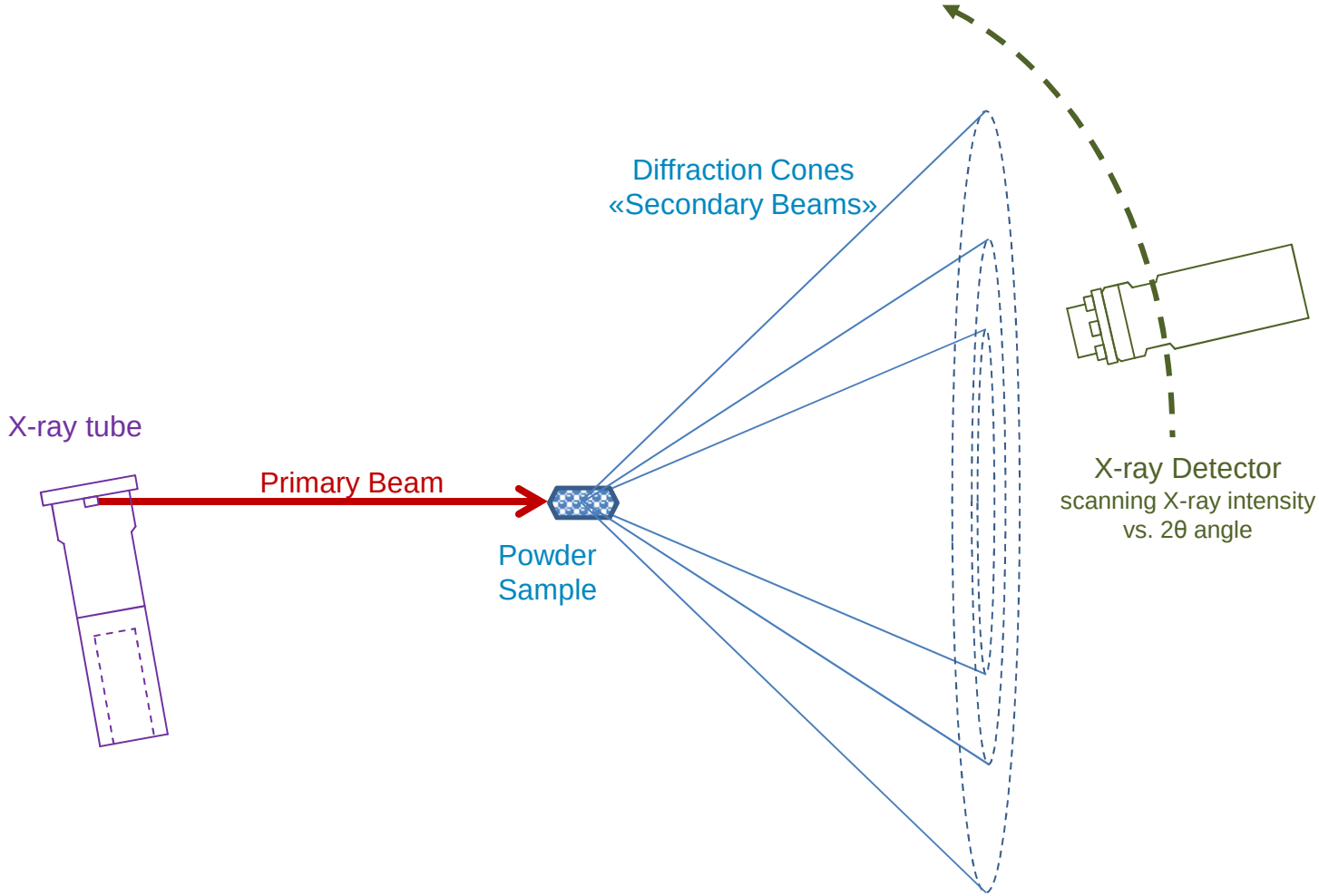
Repetition: Powder Diffraction

$$n \cdot \lambda = 2 \cdot d \cdot \sin(\theta)$$





Repetition: Powder Diffractometer

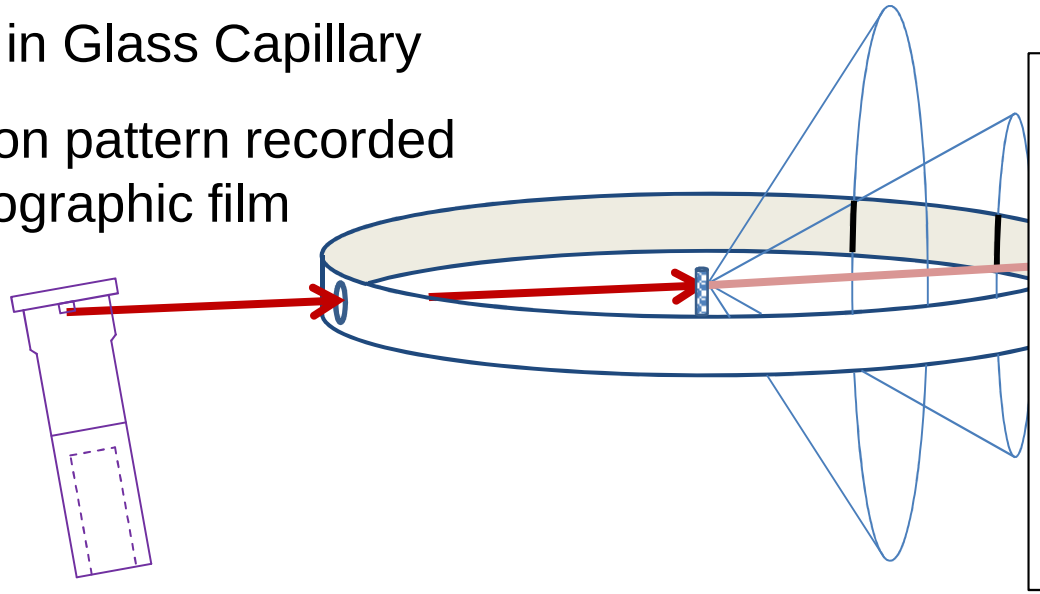


Analogue Cameras

Debye-Scherrer Camera:

Powder in Glass Capillary

Diffraction pattern recorded on photographic film



Various alternative setups:

Gandolfi …

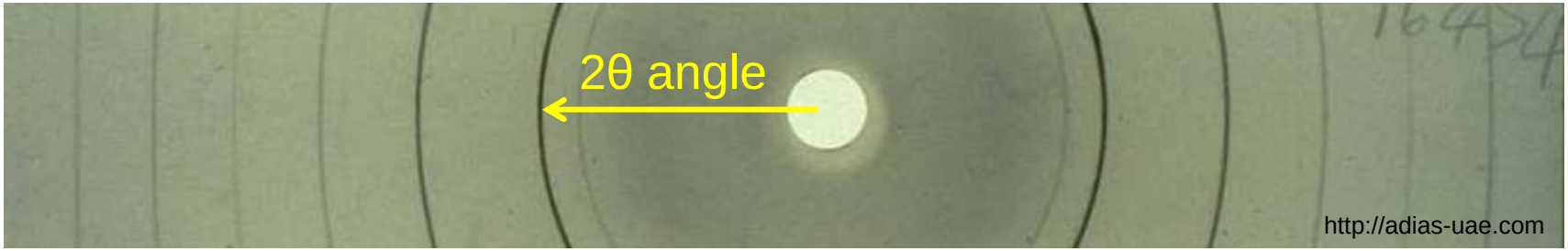
Guinier …

Straumanis …

Bradley …

Seemann-Bohlin …

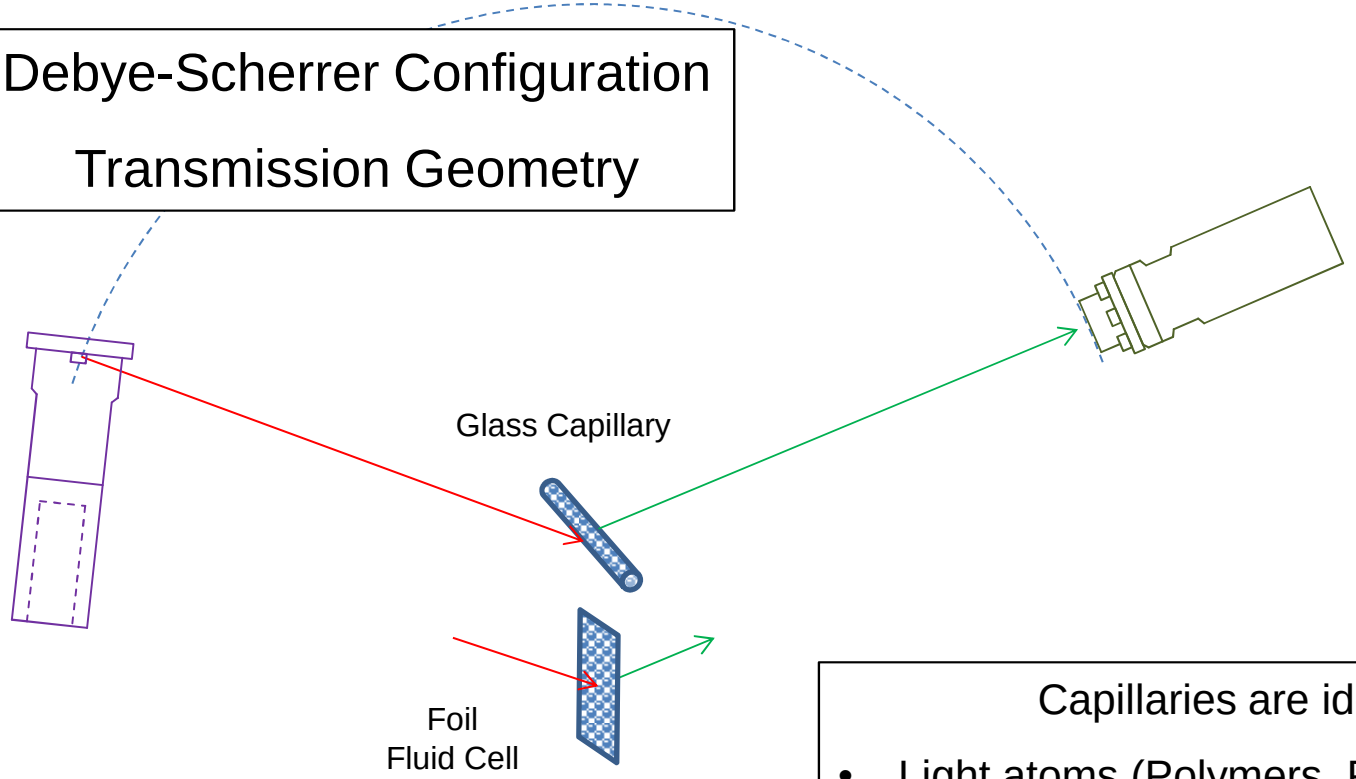
…Camera



Digital Diffractometer

Debye-Scherrer Configuration

Transmission Geometry



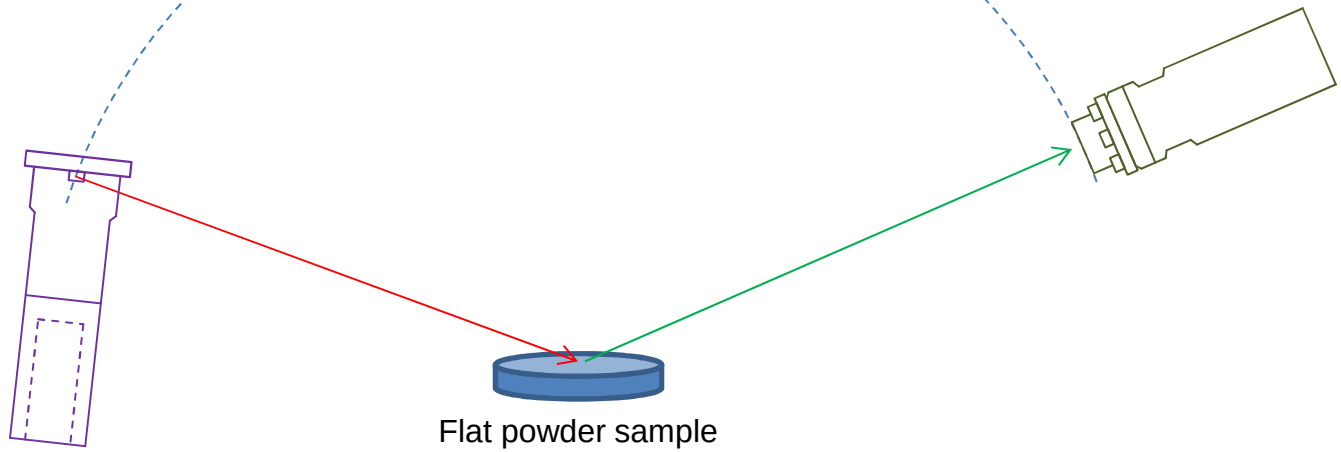
Capillaries are ideal for:

- Light atoms (Polymers, Pharmaceuticals)
- Small amounts
- Hazardous materials
- Air-sensitive materials

Bragg-Brentano Diffractometer

Bragg-Brentano Configuration

Reflective Geometry



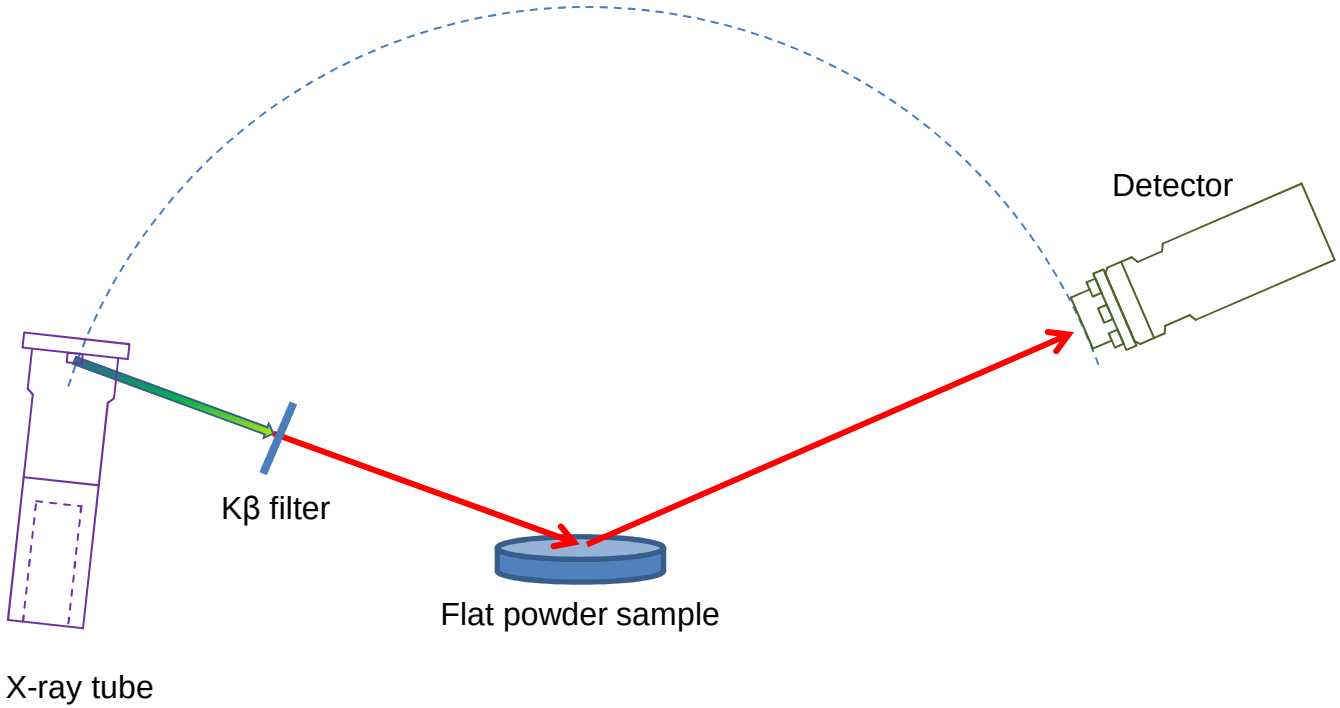
Reflective Geometry is ideal for:

- Absorbing materials (Ceramics, Metals)
- Thin films
- Texture analysis

Instruments

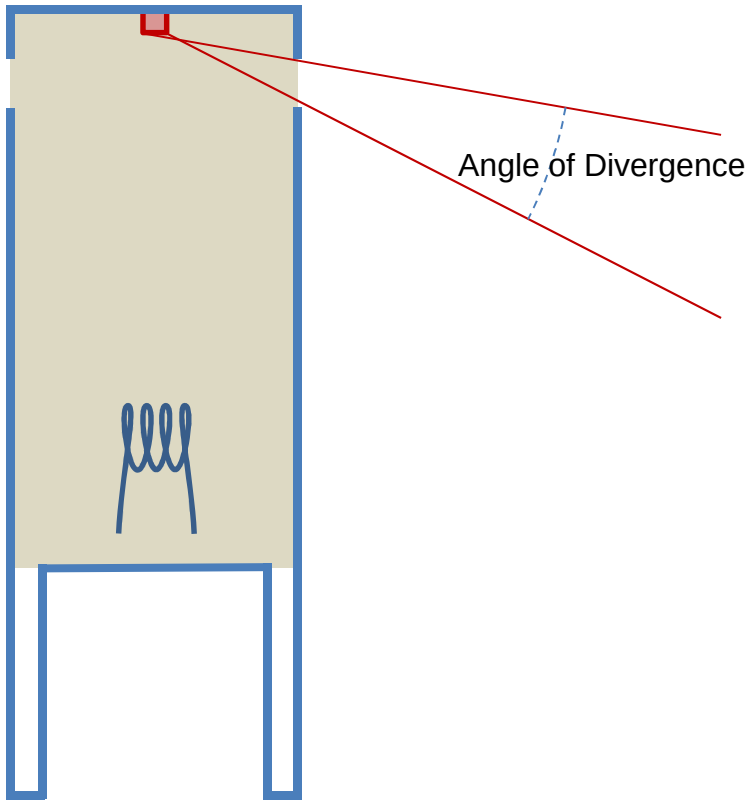
Lab	Instrument	Monochromator	Configuration
RTU	Rigaku Ultima+	Graphite Monochromator	Bragg-Brentano (Reflection)
RTU	Panalytical X'Pert	Ni-Filter	Bragg-Brentano (Reflection)
LU	Bruker D8	Ni-Filter	Bragg-Brentano (Reflection)
Uppsala Uni	Bruker D8	Ni-Filter	Bragg-Brentano (Reflection)
RTU Salaspils	Bruker D8	Energy-dispersive Detector	Bragg-Brentano (Reflection)
RMS (Uni Bern)	Panalytical X'Pert	Ni-Filter	Bragg-Brentano (Reflection)
RMS (Uni Bern)	Panalytical CubiX	Graphite Monochromator	Bragg-Brentano (Reflection)

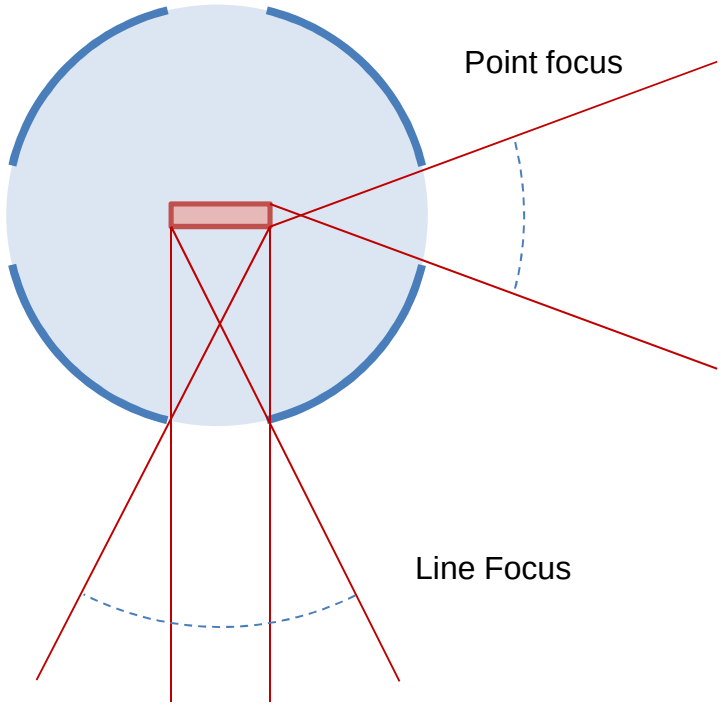
Bragg-Brentano Diffractometer



More optical elements are required to control the beam pattern.

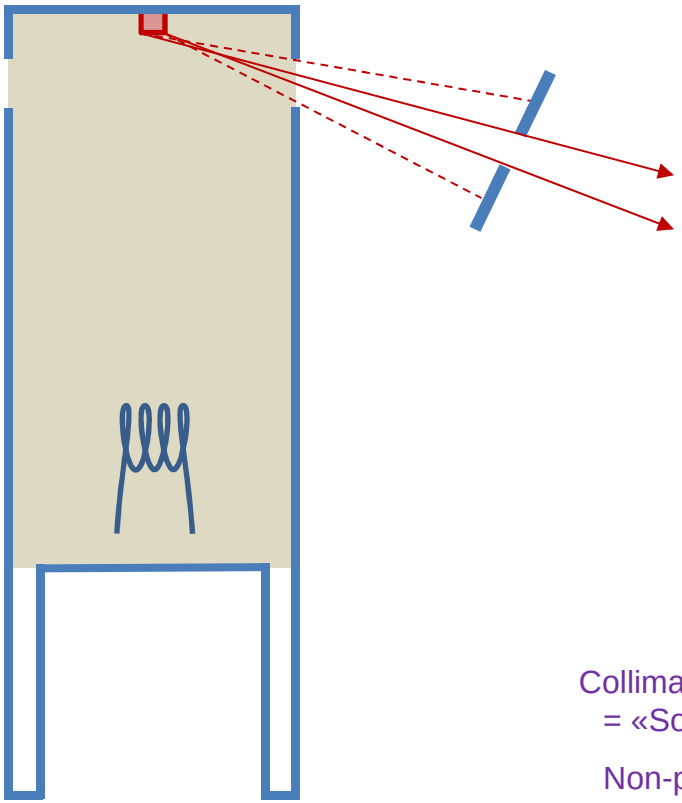
Beam Divergence



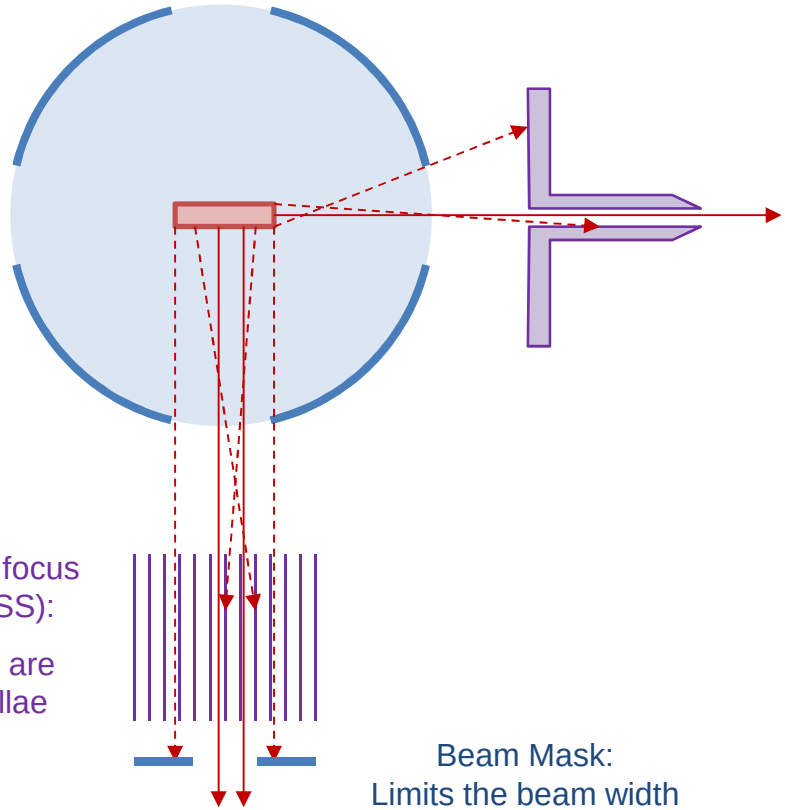


Beam Divergence

Limiting vertical divergence
with a «divergence slit» (DS)



Limiting horizontal divergence
with a «Collimator»

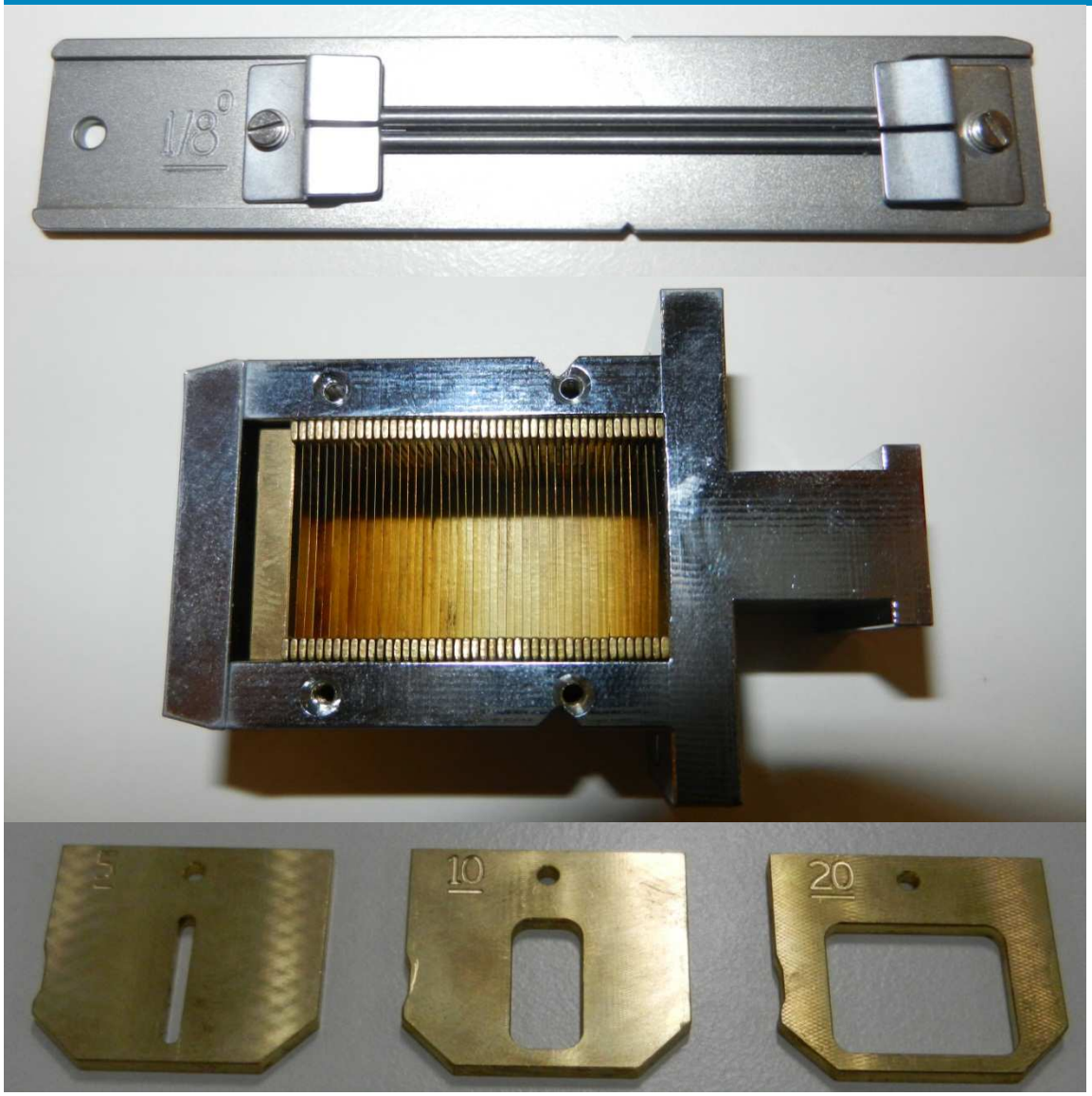


Collimator for Line focus
= «Soller Slits» (SS):

Non-parallel rays are
blocked by lamellae

Beam Mask:
Limits the beam width

Beam Divergence

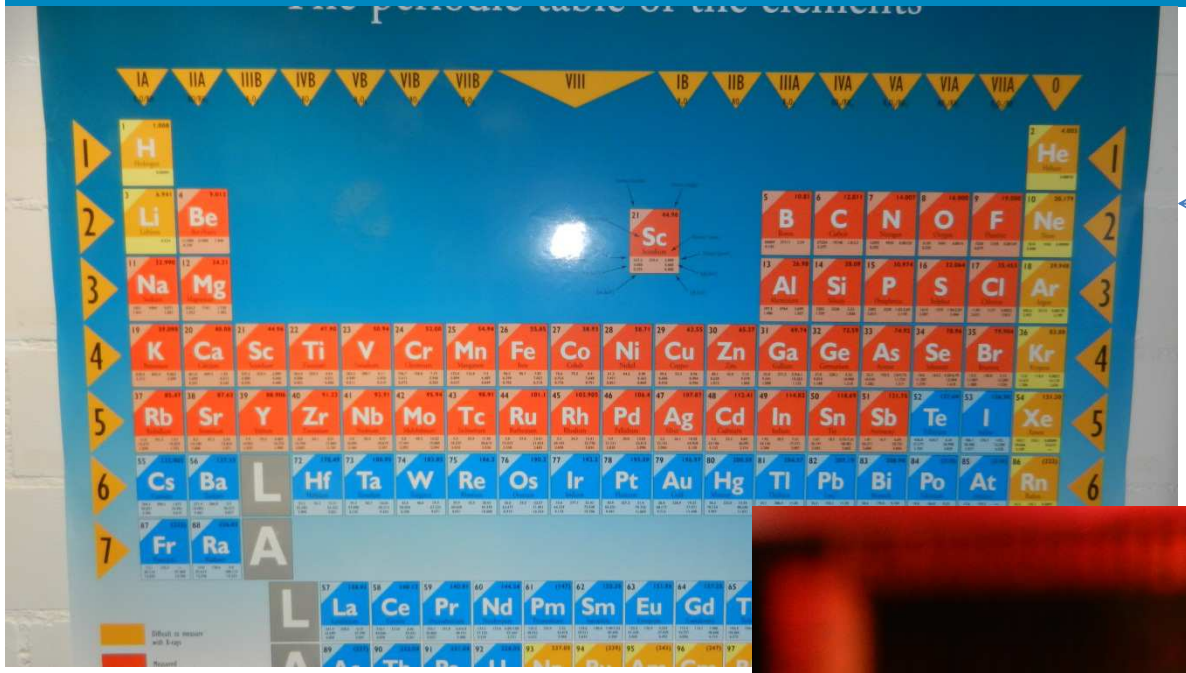


Divergence Slit

Soller Slit

Beam Masks

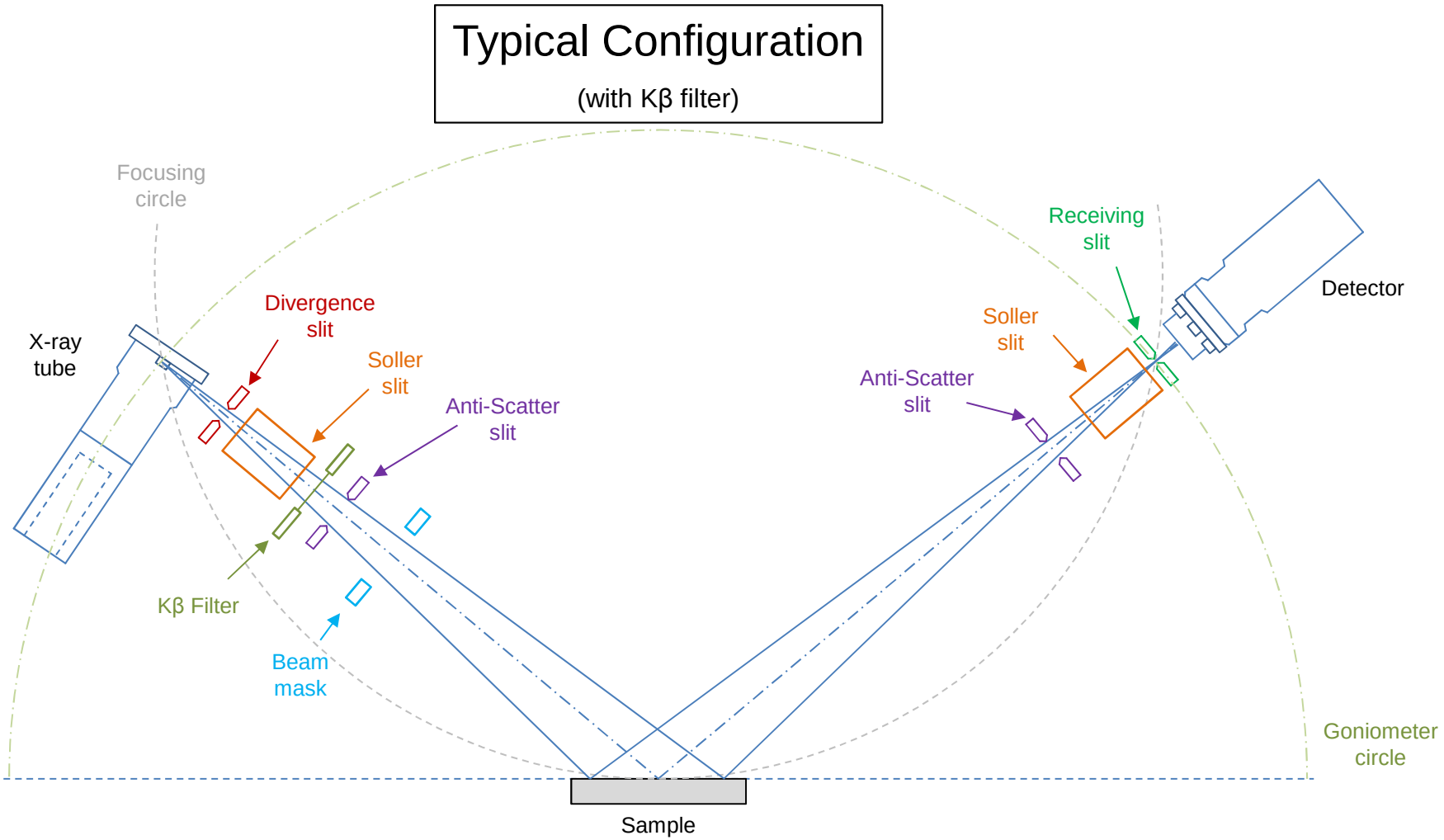
Soller Slits



Poster

Viewed through Soller Slit

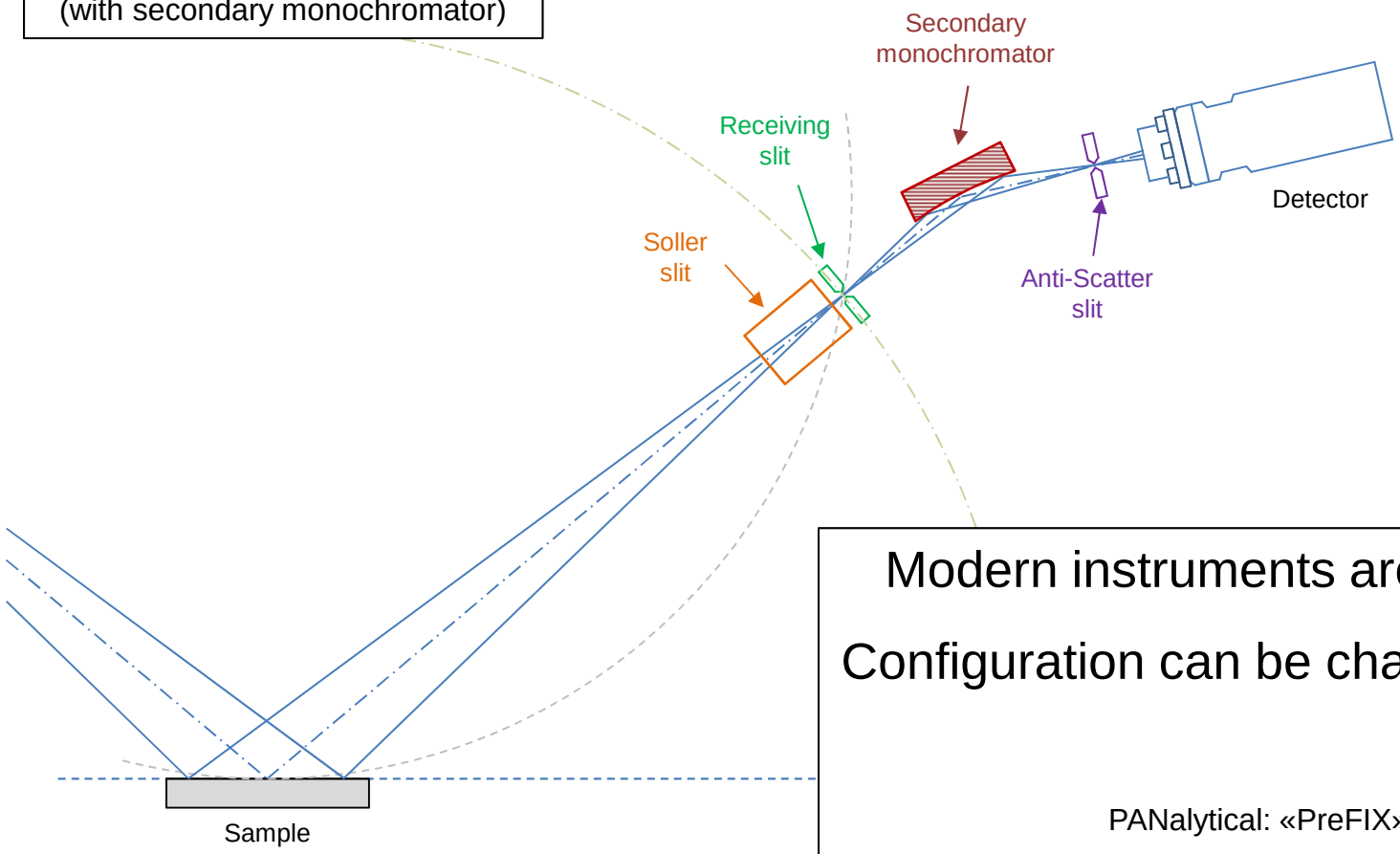
Bragg-Brentano Parafocusing Diffractometer



Bragg-Brentano Parafocusing Diffractometer

Typical Configuration

(with secondary monochromator)



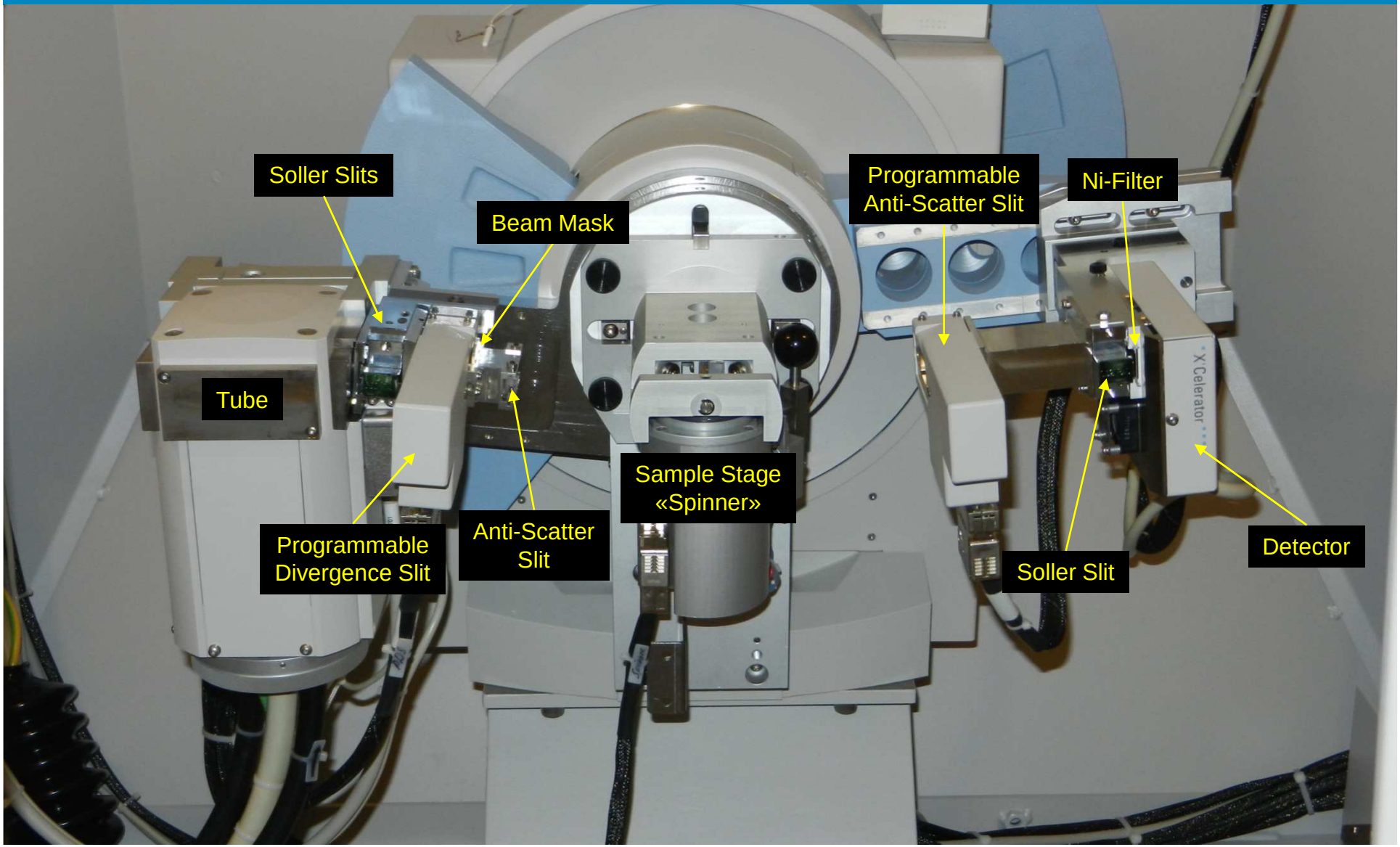
Modern instruments are modular.

Configuration can be changed easily.

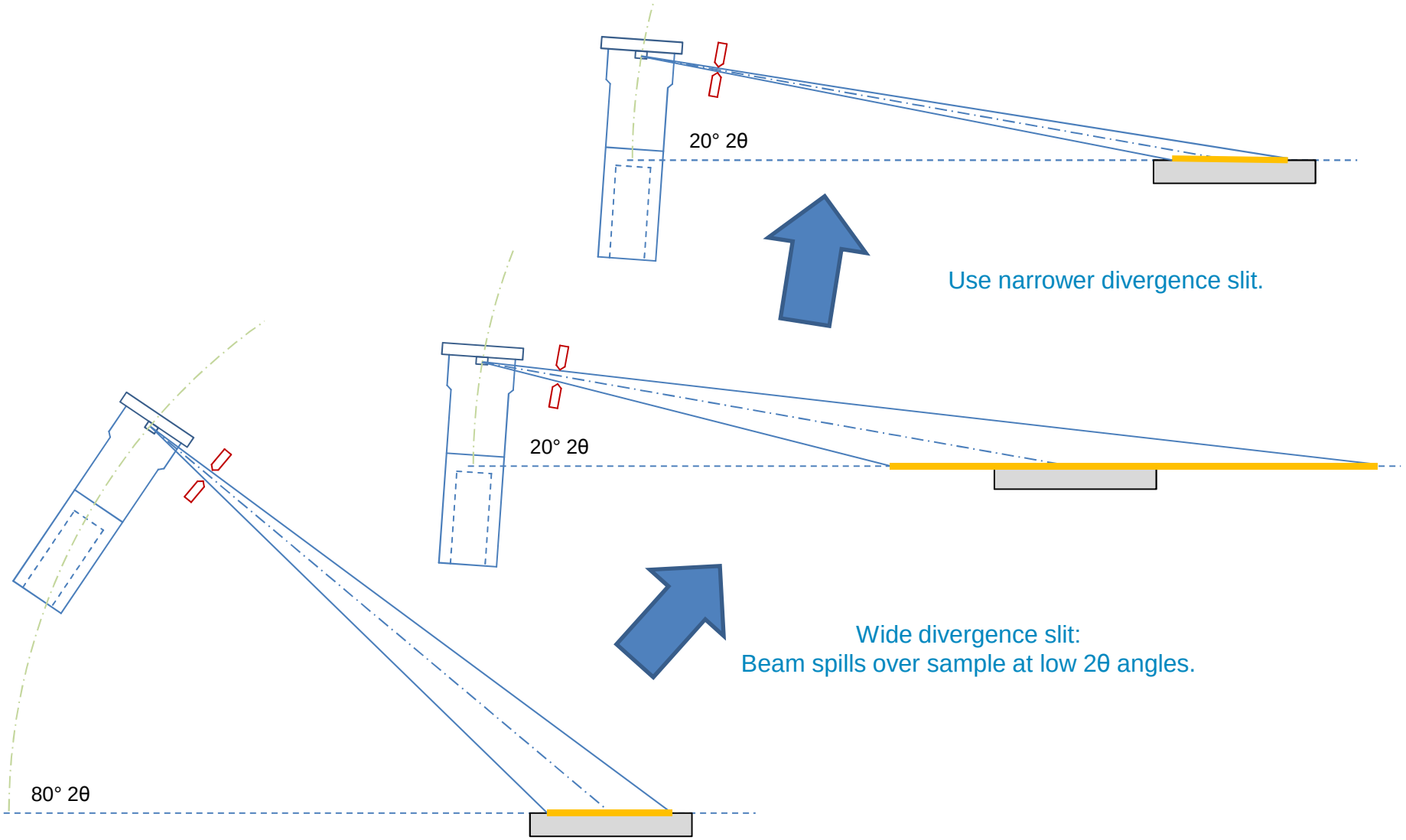
PANalytical: «PreFIX»

Bruker: «SNAP-LOCK»

Example: PANalytical X'Pert Pro MPD

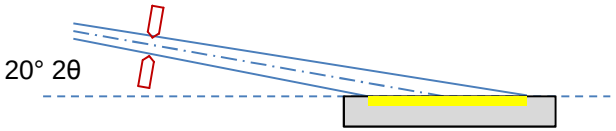


Optimum Settings: Divergence Slit



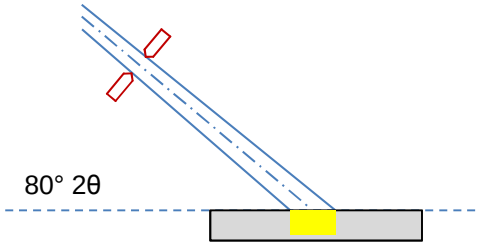
Optimum Settings: Divergence Slit

Fixed divergence slit:



Low incident angle:

- Low penetration depth
- Large illuminated area



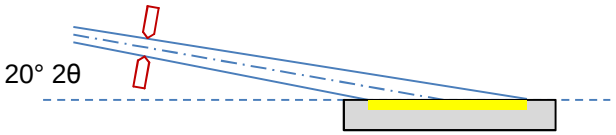
High incident angle:

- Deep penetration depth
- Small illuminated area

Irradiated **Volume** is constant

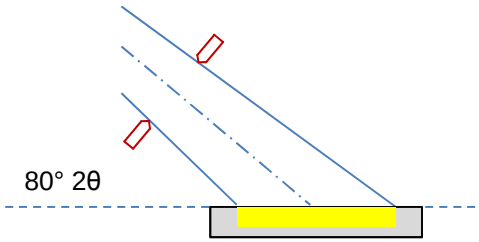
Constant intensity of diffraction pattern

Variable divergence slit:



Low incident angle:

- Narrow divergence slit
- Low penetration depth



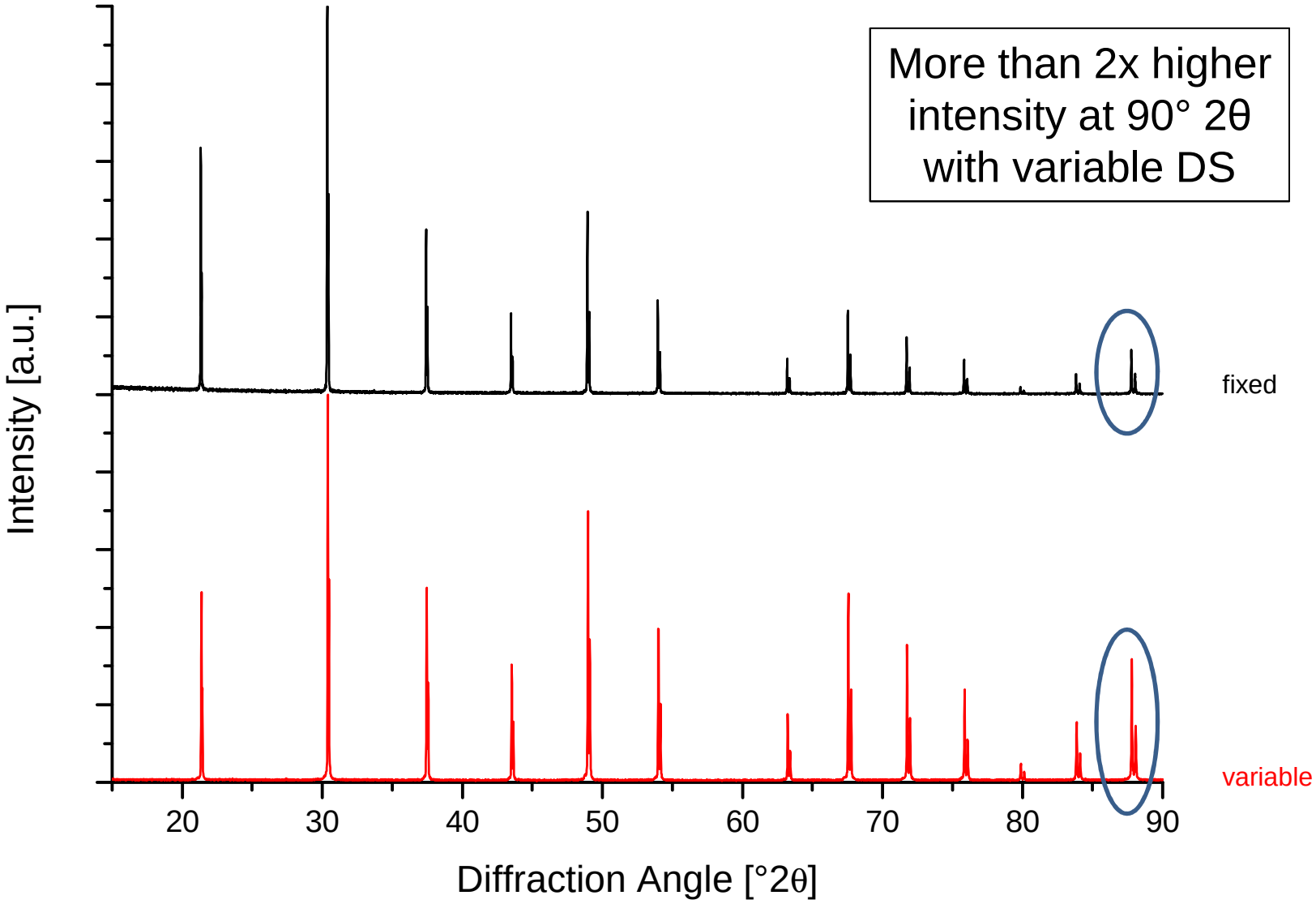
High incident angle:

- Wide divergence slit
- Deep penetration depth

Irradiated **Area** is constant

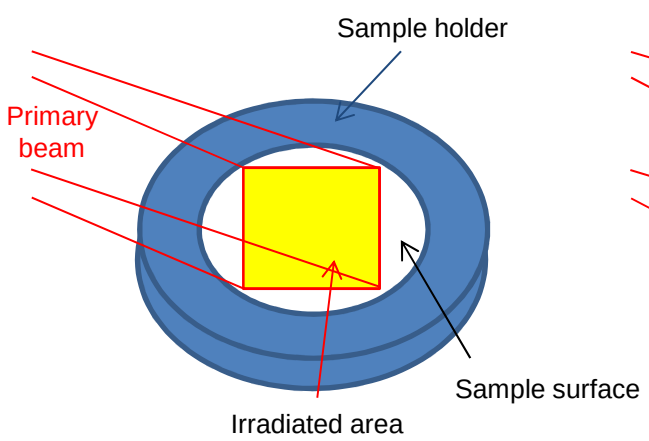
Higher diffracted intensity at high 2θ angle

Fixed vs. Variable Divergence Slit

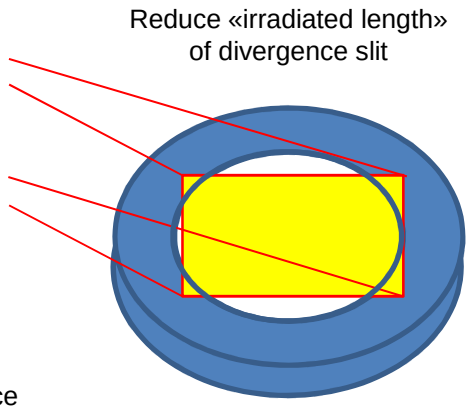


Optimum Settings: Divergence Slit

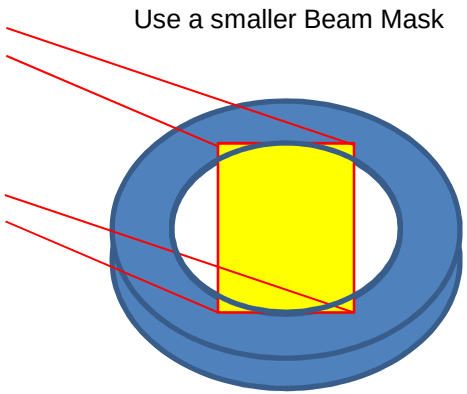
Correct!



Wrong!



Wrong!



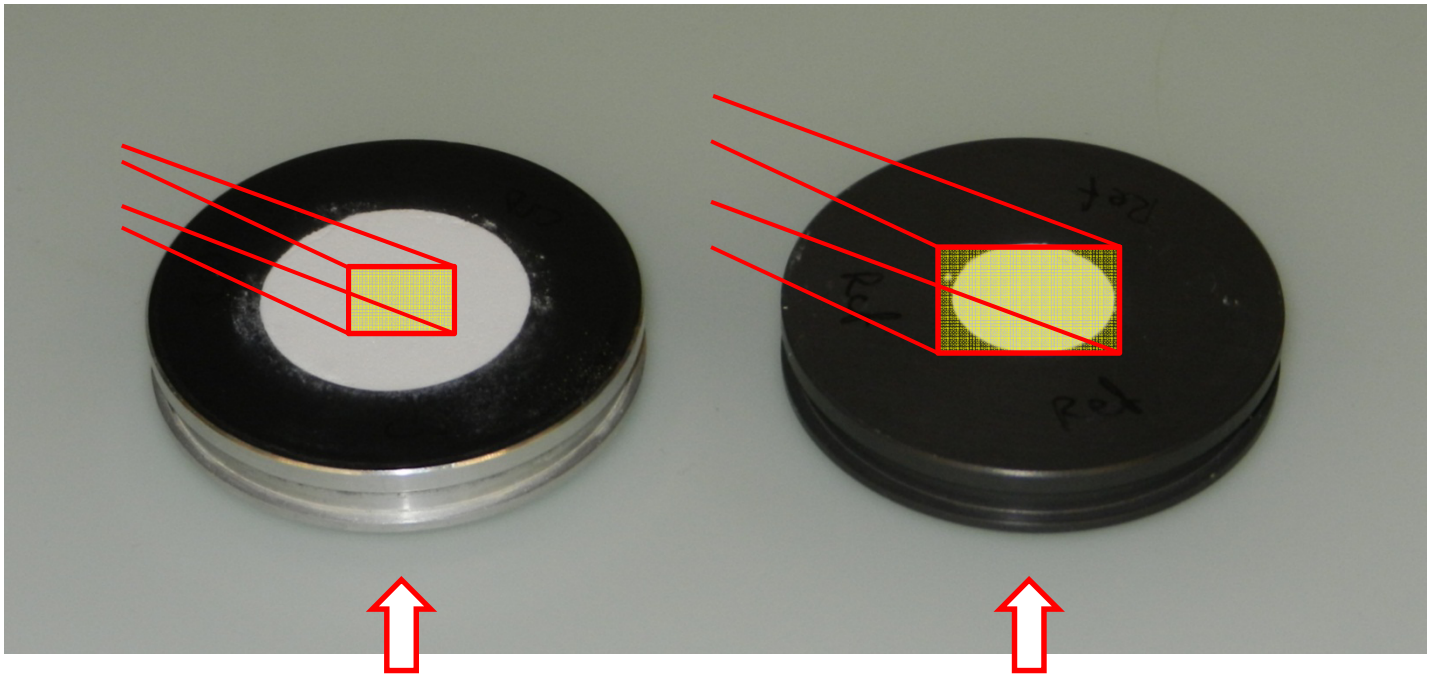
Recommendation:

- Set divergence slit to «variable»
- Adjust «irradiated length» and beam mask for maximum illumination
- But avoid beam spill-over!

Optimum Settings: Divergence Slit

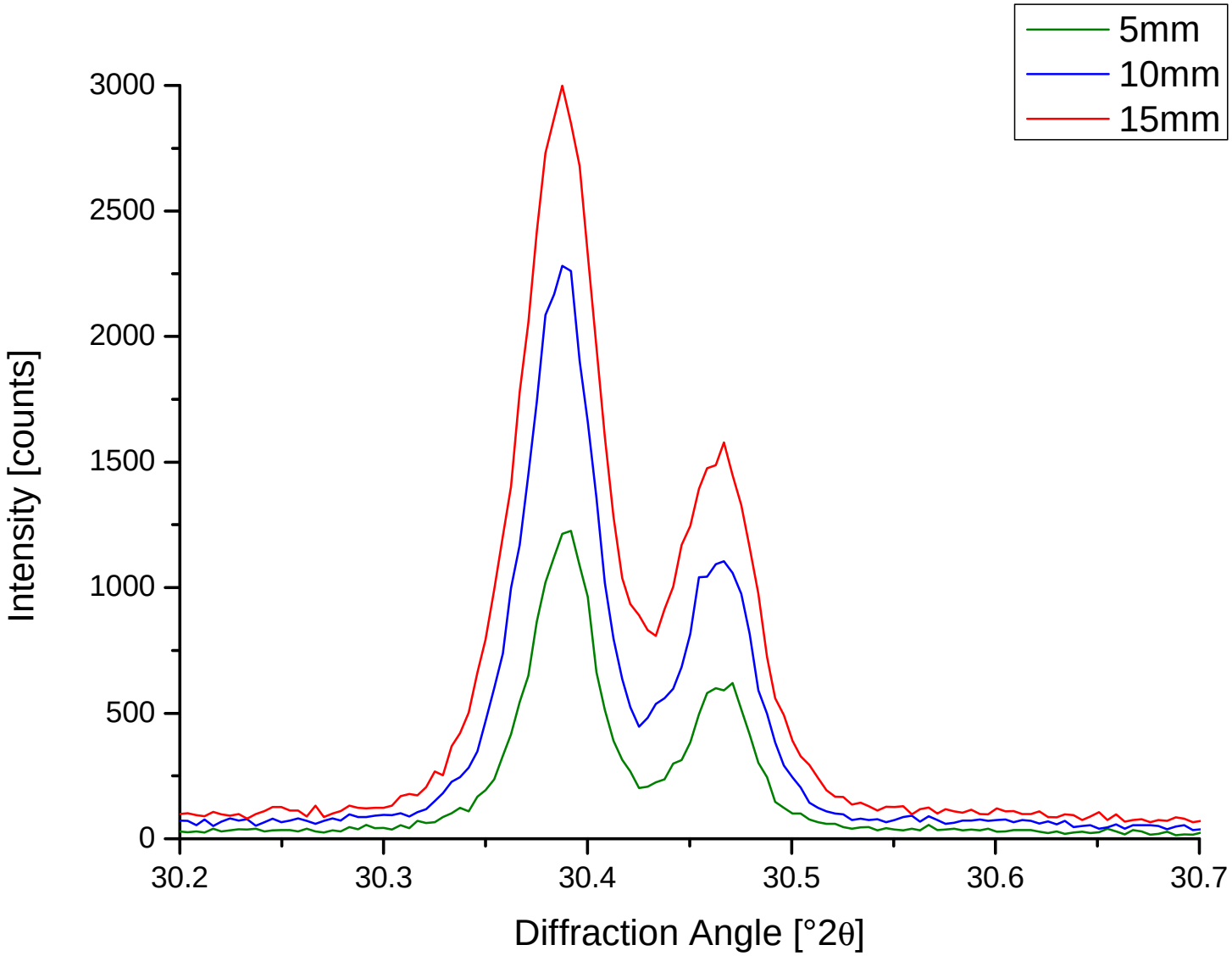
Using sample holders of various sizes?

⇒ Match your Divergence Slit and Beam Mask!



Or else: Waste of intensity or Beam spill-over

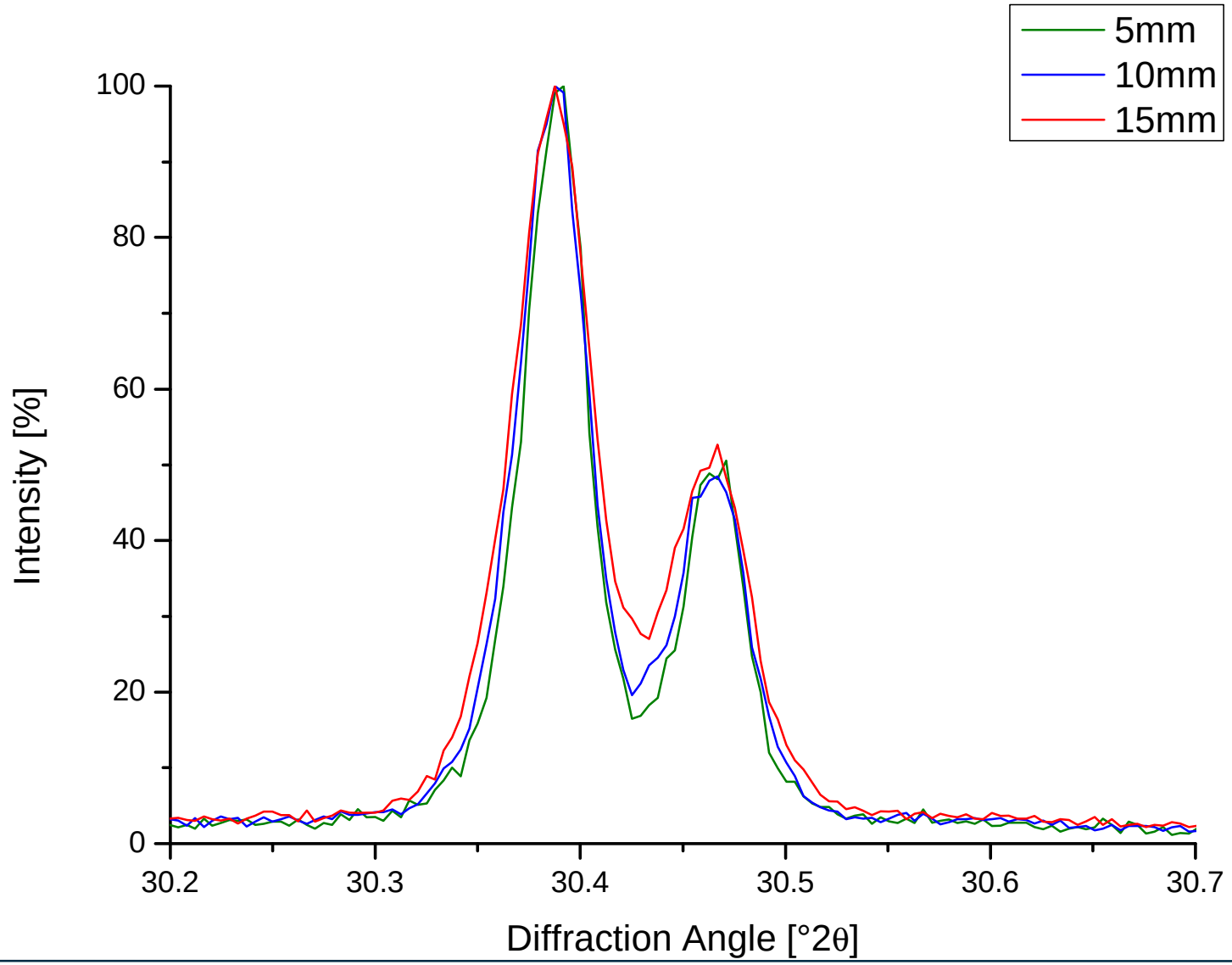
Variable Divergence Slit: Irradiated Length



Soller Slits: 0.02 rad

Beam Mask: 10mm

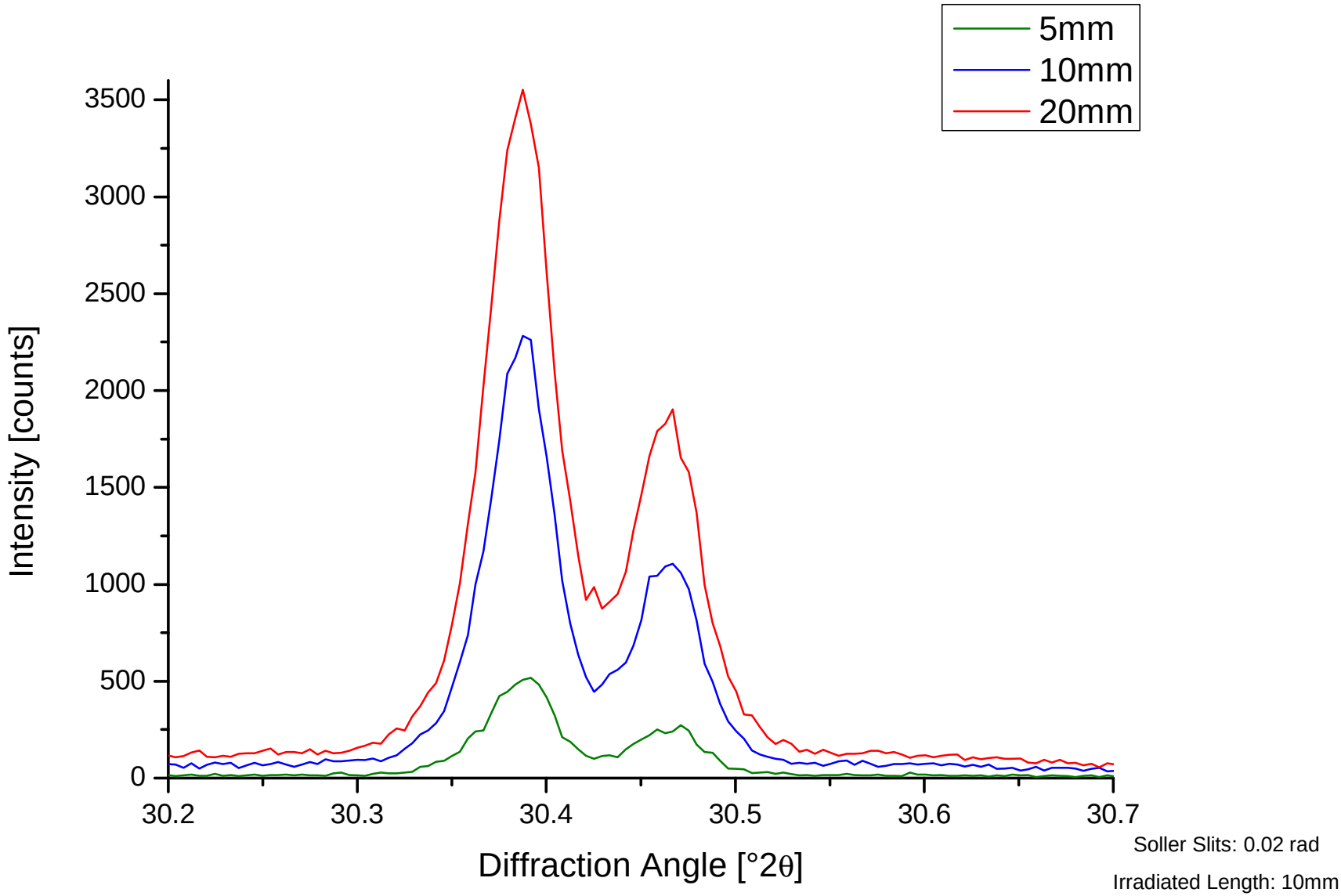
Variable Divergence Slit: Irradiated Length



Soller Slits: 0.02 rad

Beam Mask: 10mm

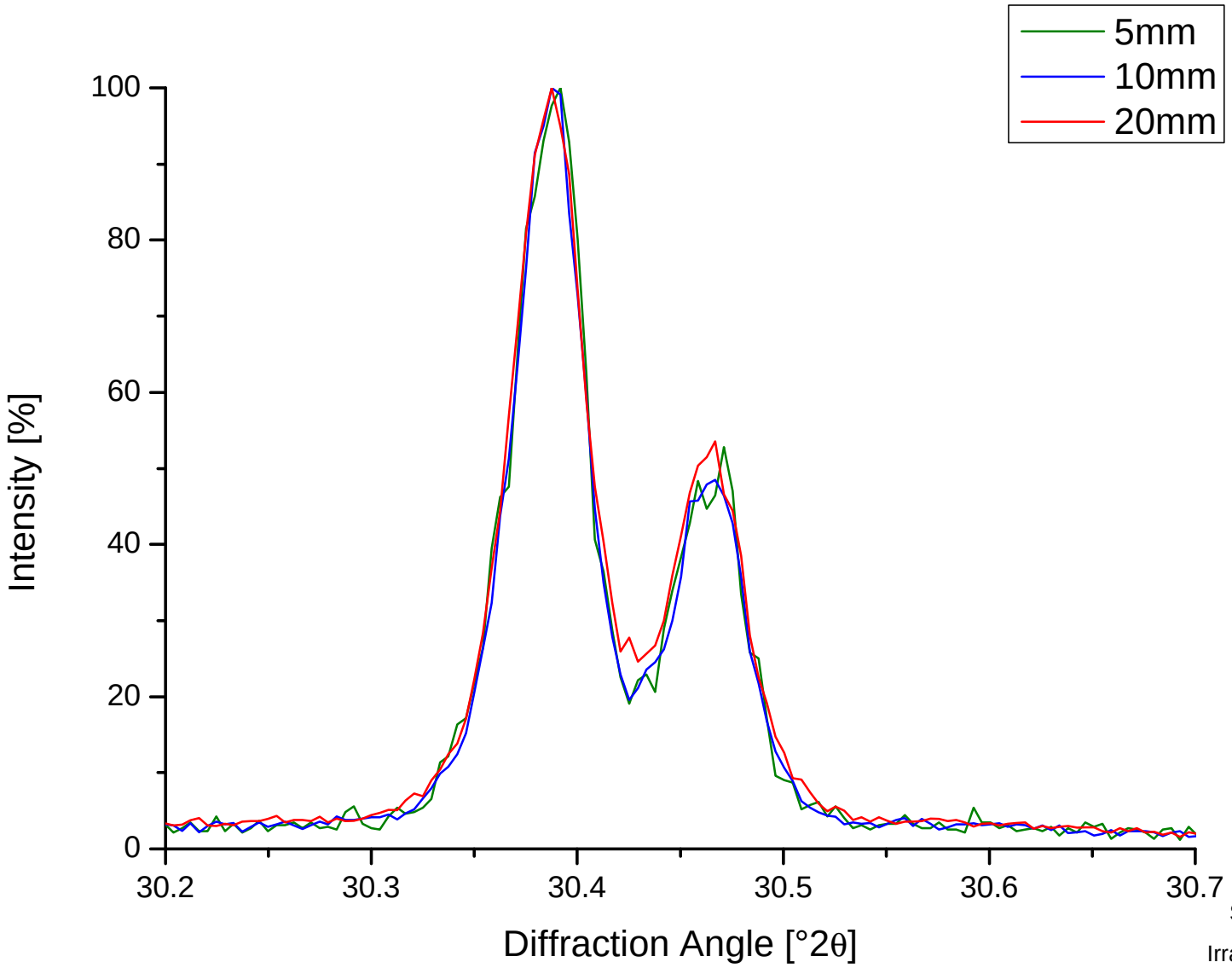
Beam Mask



Soller Slits: 0.02 rad

Irradiated Length: 10mm

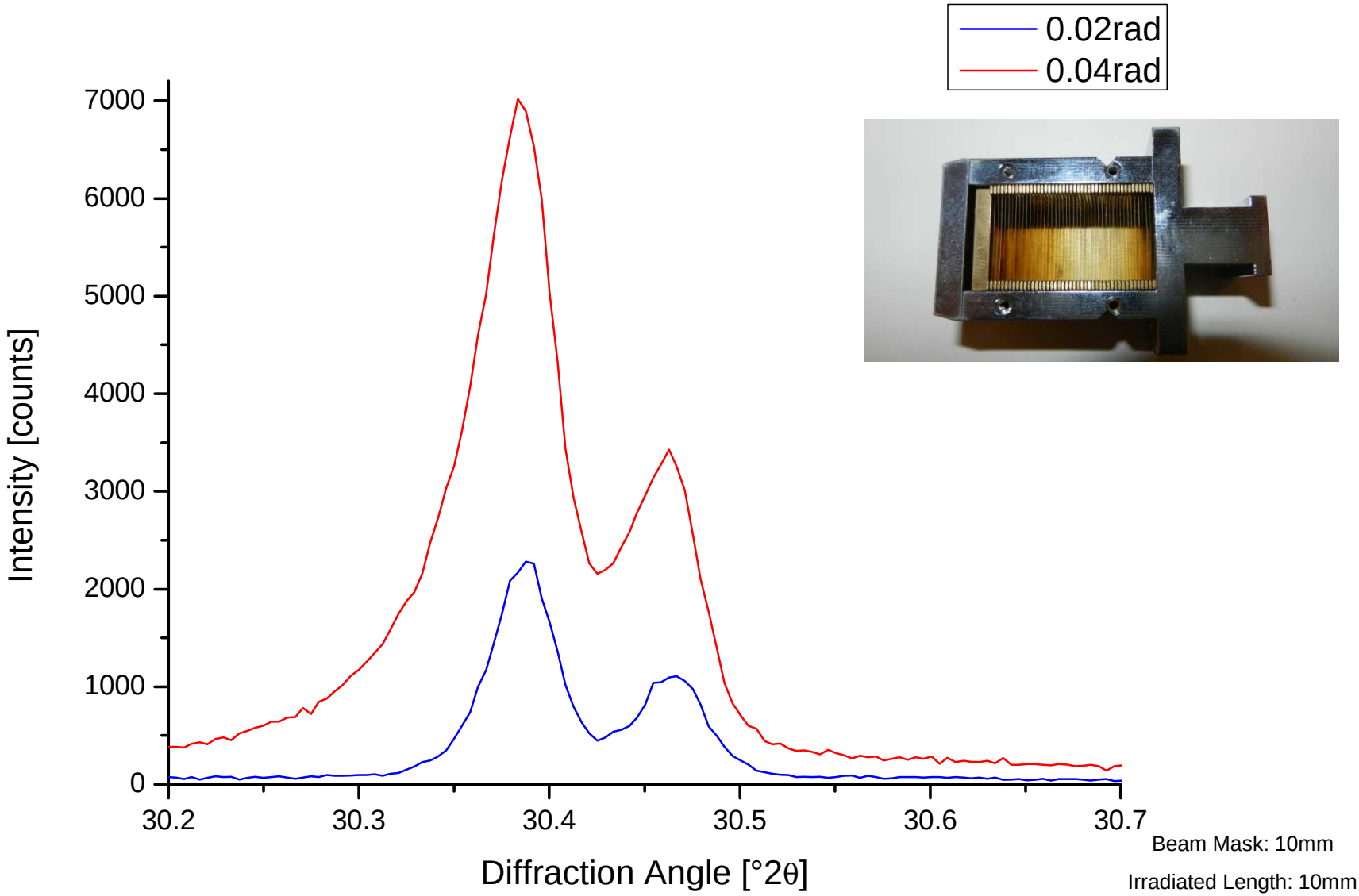
Beam Mask



Soller Slits: 0.02 rad

Irradiated Length: 10mm

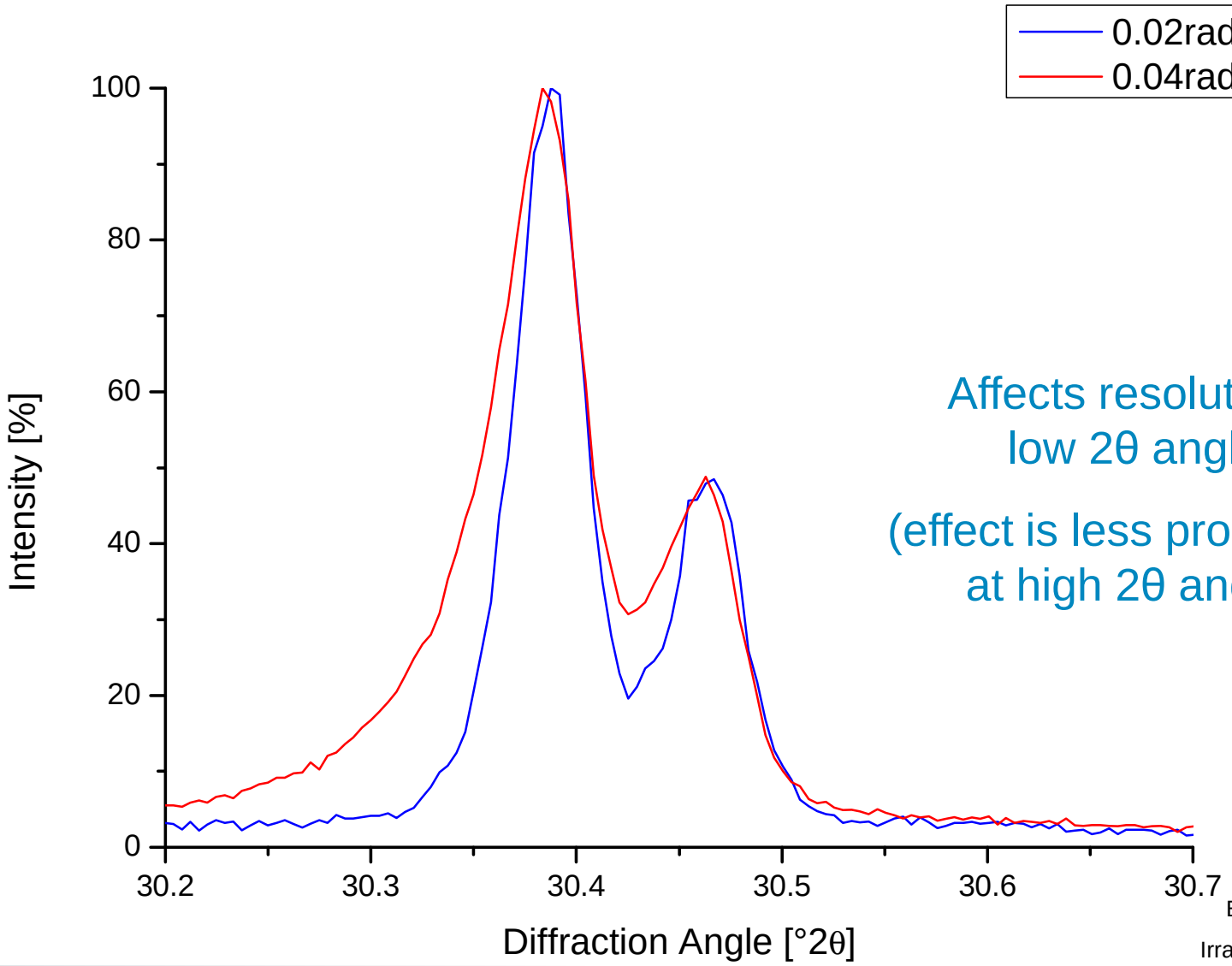
Soller Slits



Beam Mask: 10mm

Irradiated Length: 10mm

Soller Slits



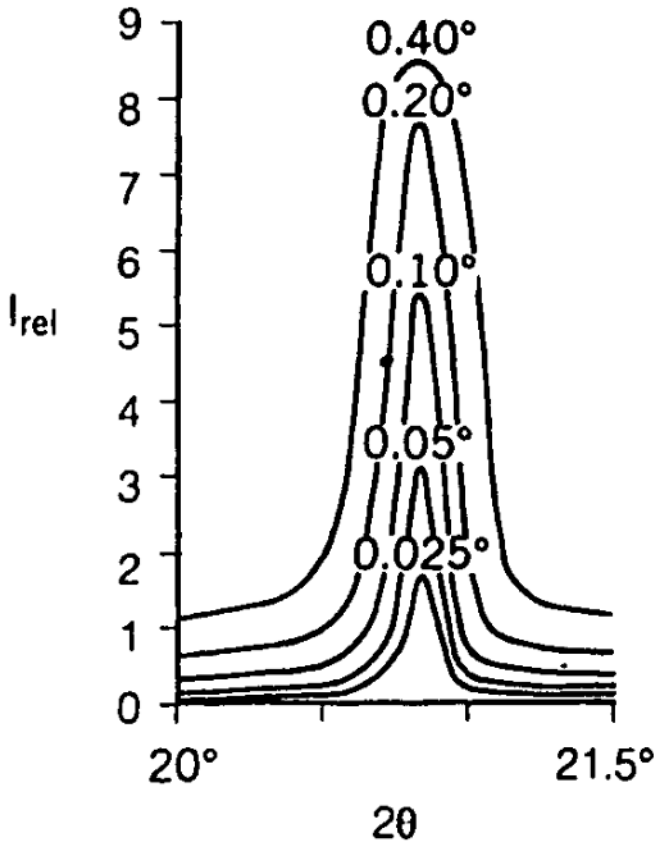
Affects resolution at low 2θ angles

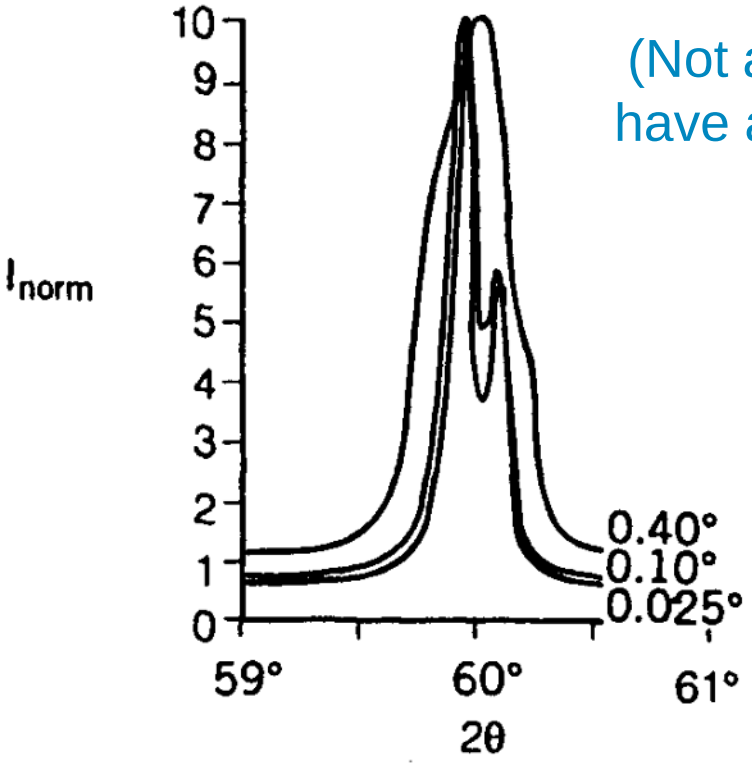
(effect is less pronounced at high 2θ angles)

Beam Mask: 10mm

Irradiated Length: 10mm

Receiving Slit





Strongly affects the resolution.

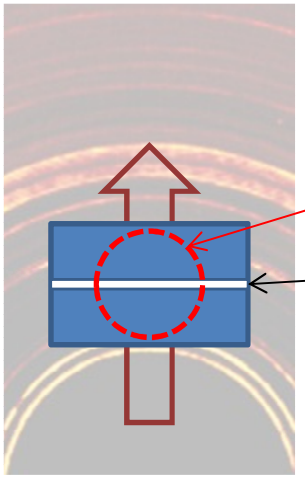
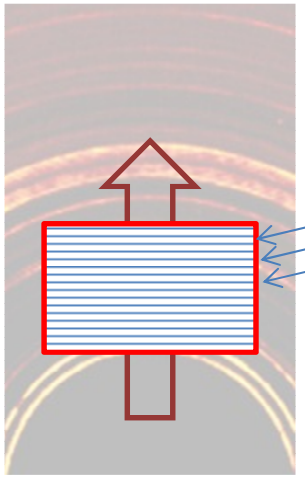
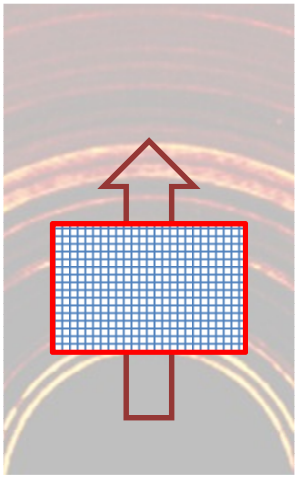
(Not all instruments have a receiving slit)

Parrish, W. Advances in X-ray diffractometry of clay minerals. X-ray analysis papers (W. Parrish, ed.), pp. 105-129. Centrex, Eindhoven, The Netherlands, 1965.

Summary: Optical Elements

Optical Element	Effect	Too Small	Too Large
Divergence Slit	Adjusts beam length on the sample	Loss of intensity	Beam spills over sample
Soller Slit	Reduces peak asymmetry	Loss of intensity, Better resolution	More asymmetry, Less resolution
Anti-Scatter Slit	Reduces background signal	Loss of intensity	High background
Beam Mask	Adjusts beam width on the sample	Loss of intensity	Beam spills over sample
Receiving Slit	Adjusts peak width / resolution	Loss of intensity Better resolution	Loss of resolution Higher intensity
Kβ Filter	Reduces Kβ peaks	-	-
Graphite Monochromator	Eliminates Kβ peaks	-	-

Detectors

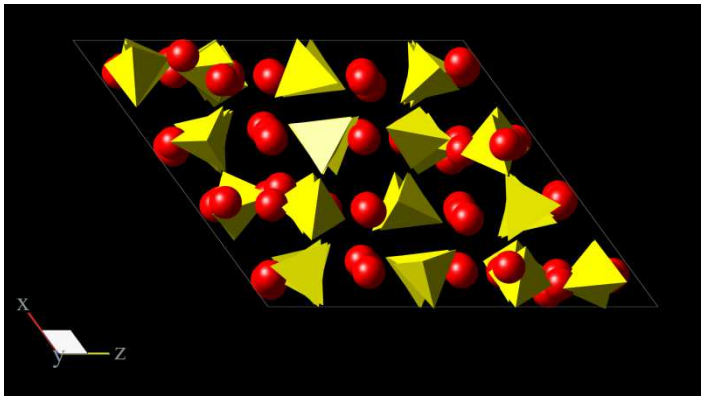
Detector Type	Point Detector (0D)	Linear Detector (1D)	Area Detector (2D)
			
	Receiving slit determines active height	Linear array of solid state detectors	2D array of solid state detectors
Example	Scintillation counter SOL-XE	X'Celerator LynxEye D/teX Ultra	PIXcel VÅNTEC
Key Features	SOL-XE: Energy dispersive	Fast Needs receiving slit! Can be set to «0D mode»	2D image of Debye rings Can be set to «1D» and «0D» mode

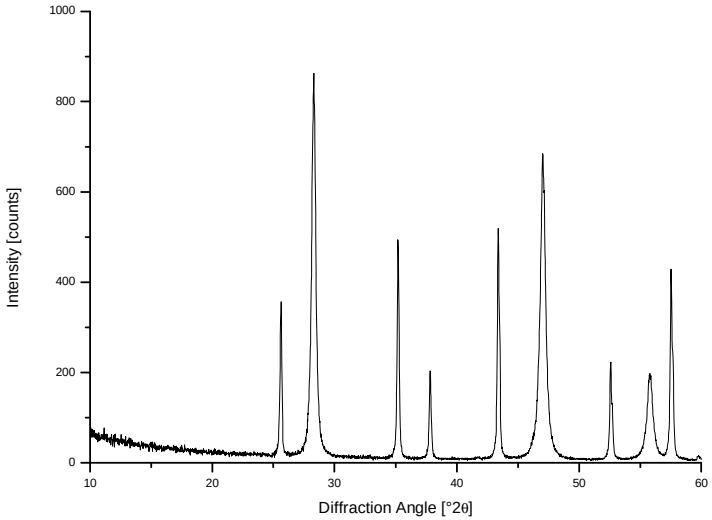
Instruments

Lab	Instrument	Monochr.	Detector
RTU	Rigaku Ultima+	Graphite	0D
RTU	Panalytical X'Pert	Ni-Filter	1D X'Celerator
LU	Bruker D8	Ni-Filter	1D LynxEye
Uppsala Uni	Bruker D8	Ni-Filter	1D LynxEye
RTU Salaspils	Bruker D8	Energy-disp. Detector	0D SOL-XE
RMS (Uni Bern)	Panalytical X'Pert	Ni-Filter	1D X'Celerator
RMS (Uni Bern)	Panalytical CubiX	Graphite	0D

Phase Identification

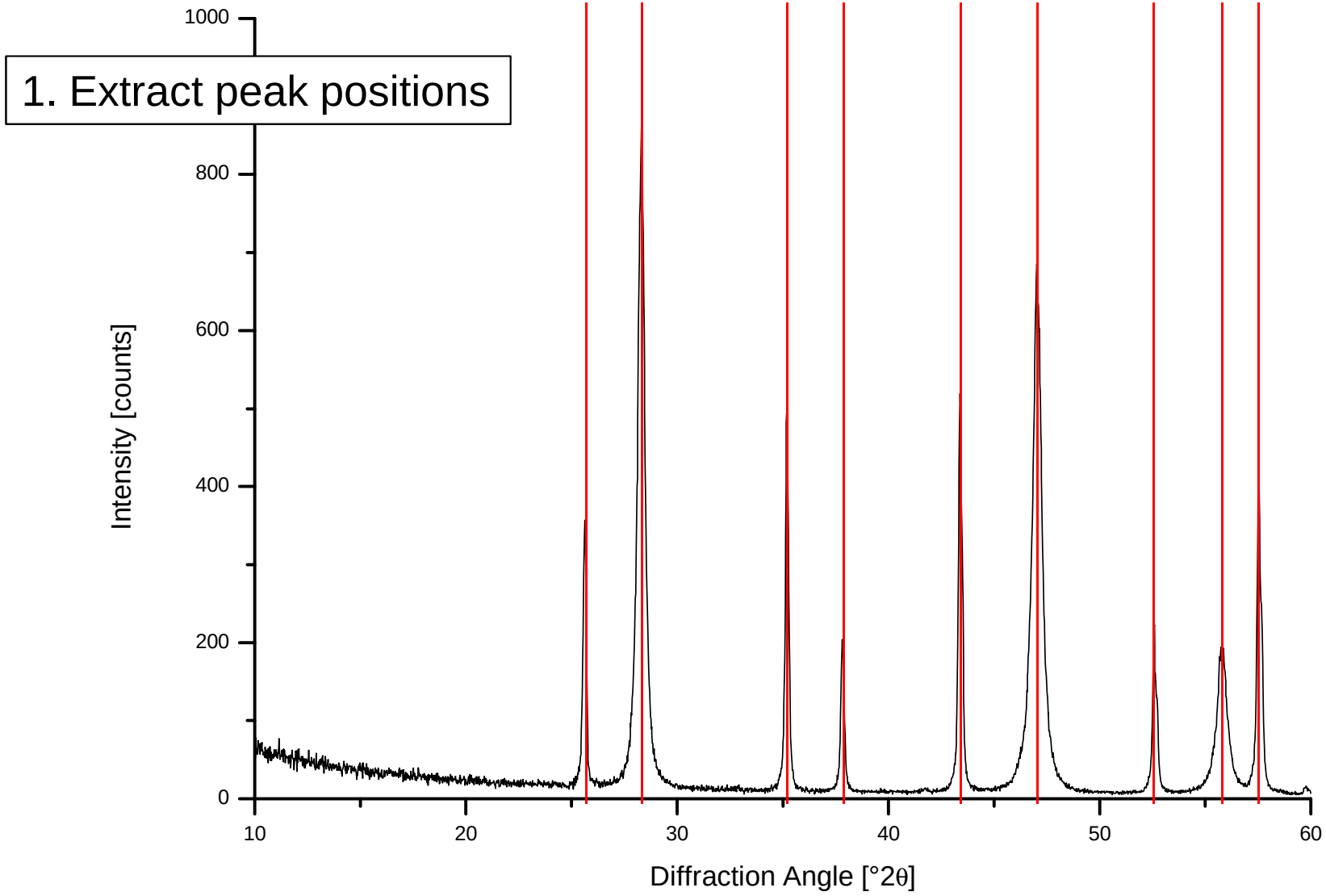
A crystal structure will generate a characteristic XRD pattern.





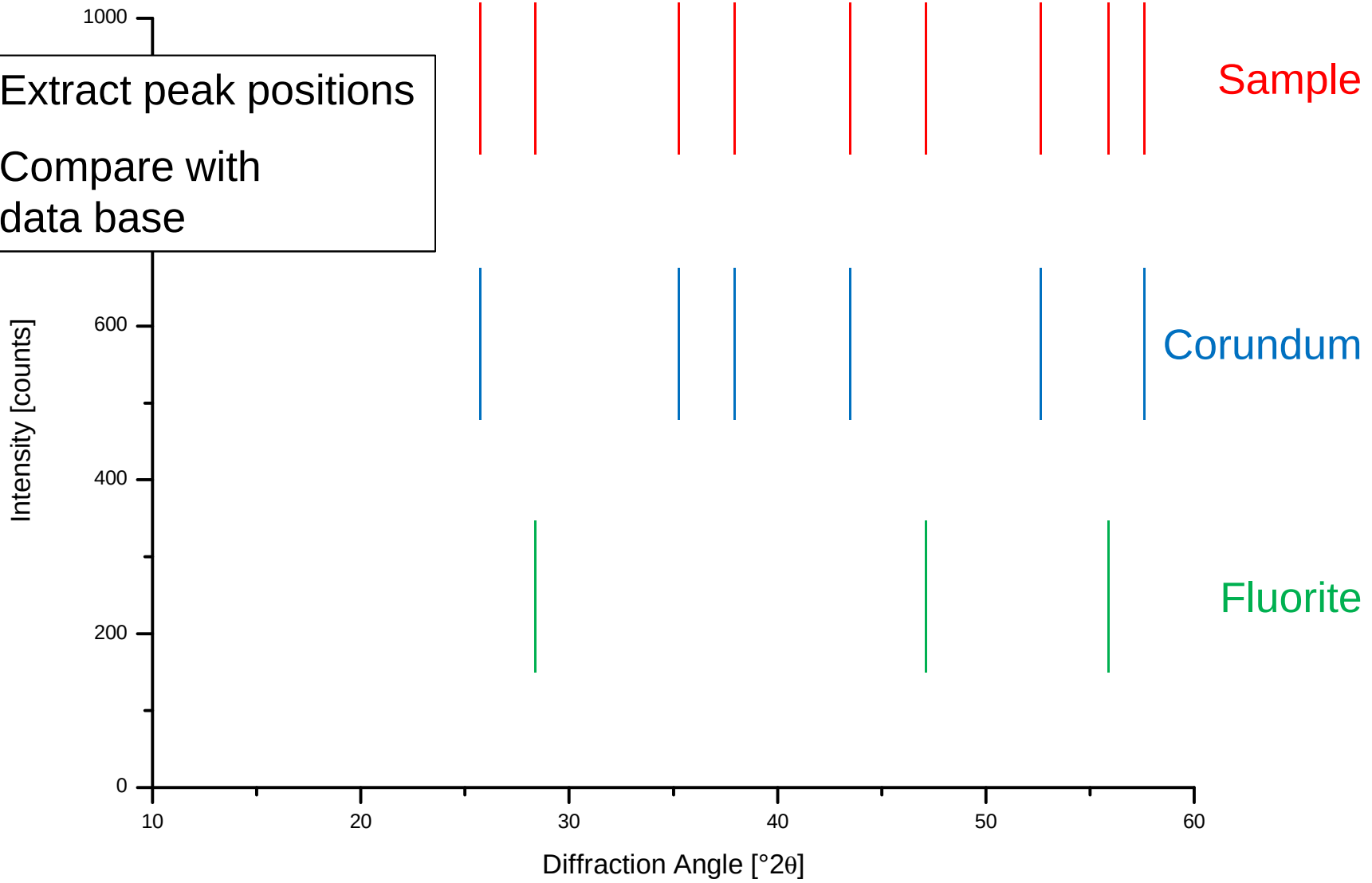
Feature	Origin
Peak positions	- Symmetry of the unit cell - Dimensions of the unit cell
Relative peak intensities	- Coordinates of atoms in unit cell - Species of atoms
Absolute peak intensities	- Abundance of phase - Primary beam intensity
Peak width	- Crystallite size - Stress/Strain in crystal lattice

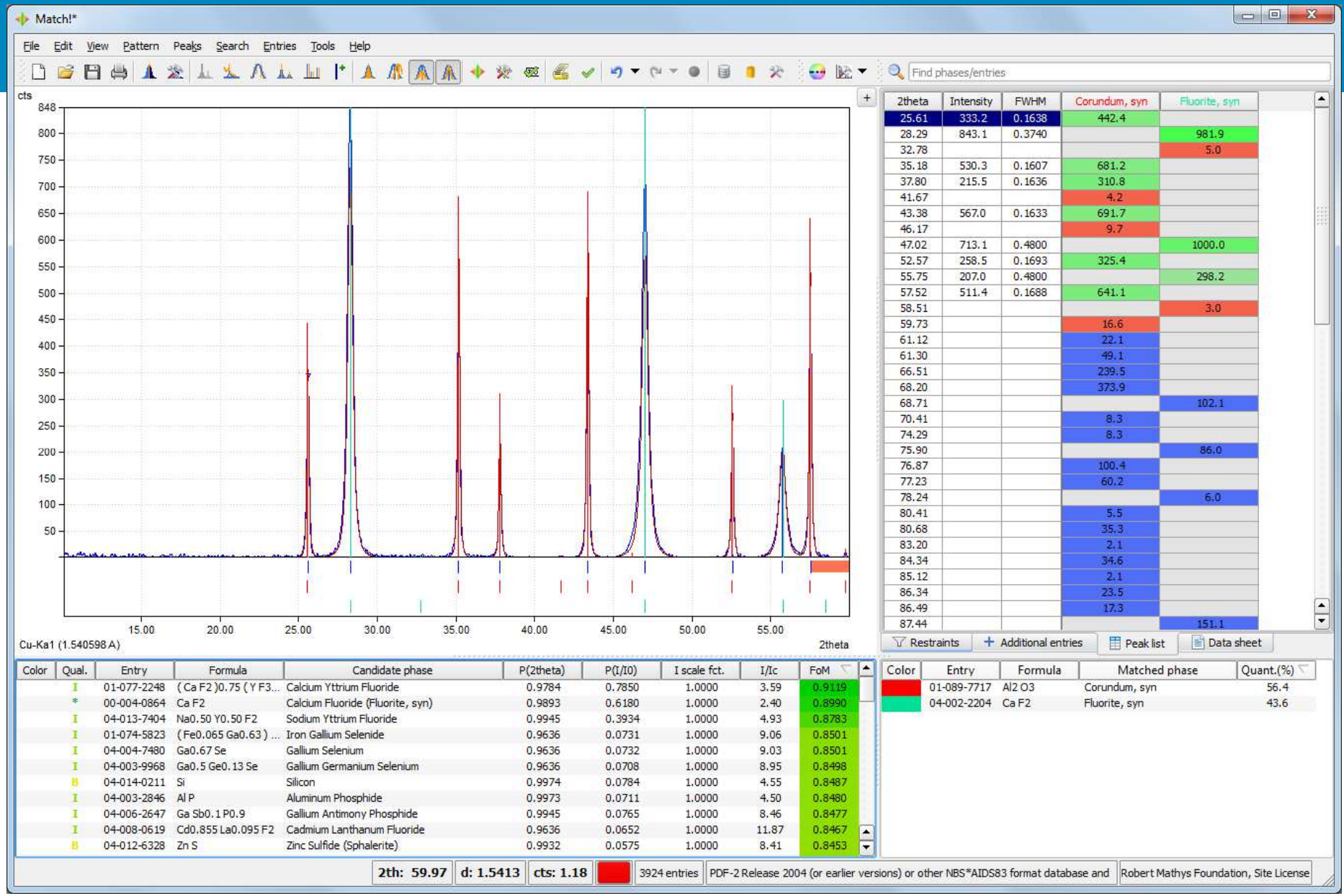
Phase Identification



Phase Identification

1. Extract peak positions
2. Compare with data base




Match!*
File Edit View Pattern Peaks Search Entries Tools Help
Find phases/entries
cts
Cu-Ka1 (1.540598 A)
2theta
2theta | Intensity | FWHM | Corundum, syn | Fluorite, syn
25.61 | 333.2 | 0.1638 | 442.4
28.29 | 843.1 | 0.3740 | 981.9
32.78 | 5.0
35.18 | 530.3 | 0.1607 | 681.2
37.80 | 215.5 | 0.1636 | 310.8
41.67 | 4.2
43.38 | 567.0 | 0.1633 | 691.7
46.17 | 9.7
47.02 | 713.1 | 0.4800 | 1000.0
52.57 | 258.5 | 0.1693 | 325.4
55.75 | 207.0 | 0.4800 | 298.2
57.52 | 511.4 | 0.1688 | 641.1
58.51 | 3.0
59.73 | 16.6
61.12 | 22.1
61.30 | 49.1
66.51 | 239.5
68.20 | 373.9
68.71 | 102.1
70.41 | 8.3
74.29 | 8.3
75.90 | 86.0
76.87 | 100.4
77.23 | 60.2
78.24 | 6.0
80.41 | 5.5
80.68 | 35.3
83.20 | 2.1
84.34 | 34.6
85.12 | 2.1
86.34 | 23.5
86.49 | 17.3
87.44 | 151.1
Restraints
Additional entries
Peak list
Data sheet
Color | Qual. | Entry | Formula | Candidate phase | P(2theta) | P(I/I0) | I scale fct. | I/Ic | FoM
I 01-077-2248 (Ca F2)0.75 (Y F3... Calcium Yttrium Fluoride 0.9784 0.7850 1.0000 3.59 0.9119
* 00-004-0864 Ca F2 Calcium Fluoride (Fluorite, syn) 0.9893 0.6180 1.0000 2.40 0.8990
I 04-013-7404 Na0.50 Y0.50 F2 Sodium Yttrium Fluoride 0.9945 0.3934 1.0000 4.93 0.8783
I 01-074-5823 (Fe0.065 Ga0.63) ... Iron Gallium Selenide 0.9636 0.0731 1.0000 9.06 0.8501
I 04-004-7480 Ga0.67 Se Gallium Selenium 0.9636 0.0732 1.0000 9.03 0.8501
I 04-003-9968 Ga0.5 Ge0.13 Se Gallium Germanium Selenium 0.9636 0.0708 1.0000 8.95 0.8498
I 04-014-0211 Si Silicon 0.9974 0.0784 1.0000 4.55 0.8487
I 04-003-2846 Al P Aluminum Phosphide 0.9973 0.0711 1.0000 4.50 0.8480
I 04-006-2647 Ga Sb0.1 P0.9 Gallium Antimony Phosphide 0.9945 0.0765 1.0000 8.46 0.8477
I 04-008-0619 Cd0.855 La0.095 F2 Cadmium Lanthanum Fluoride 0.9636 0.0652 1.0000 11.87 0.8467
I 04-012-6328 Zn S Zinc Sulfide (Sphalerite) 0.9932 0.0575 1.0000 8.41 0.8453
Color | Entry | Formula | Matched phase | Quant.(%)
01-089-7717 Al2 O3 Corundum, syn 56.4
04-002-2204 Ca F2 Fluorite, syn 43.6
2th: 59.97 d: 1.5413 cts: 1.18
3924 entries
PDF-2 Release 2004 (or earlier versions) or other NBS*AIDS83 format database and
Robert Mathys Foundation, Site License

Databases

Databases containing powder diffraction data (line positions)

Database	Publisher	# of Entries	Data sets
PDF-2	ICDD (http://www.icdd.com)	250’182	All
PDF-4+	ICDD (http://www.icdd.com)	328’660	Inorganic
PDF-4/Minerals	ICDD (http://www.icdd.com)	39’410	Minerals (Subset of PDF-4+)
PDF-4/Organics	ICDD (http://www.icdd.com)	471’257	Organics
COD	COD http://www.crystallography.net	215’708	All (excl. biopolymers)

Commercial

Open Access

(Received funding by Research Council of Lithuania (2010-2011))

Programmes for Search / Match

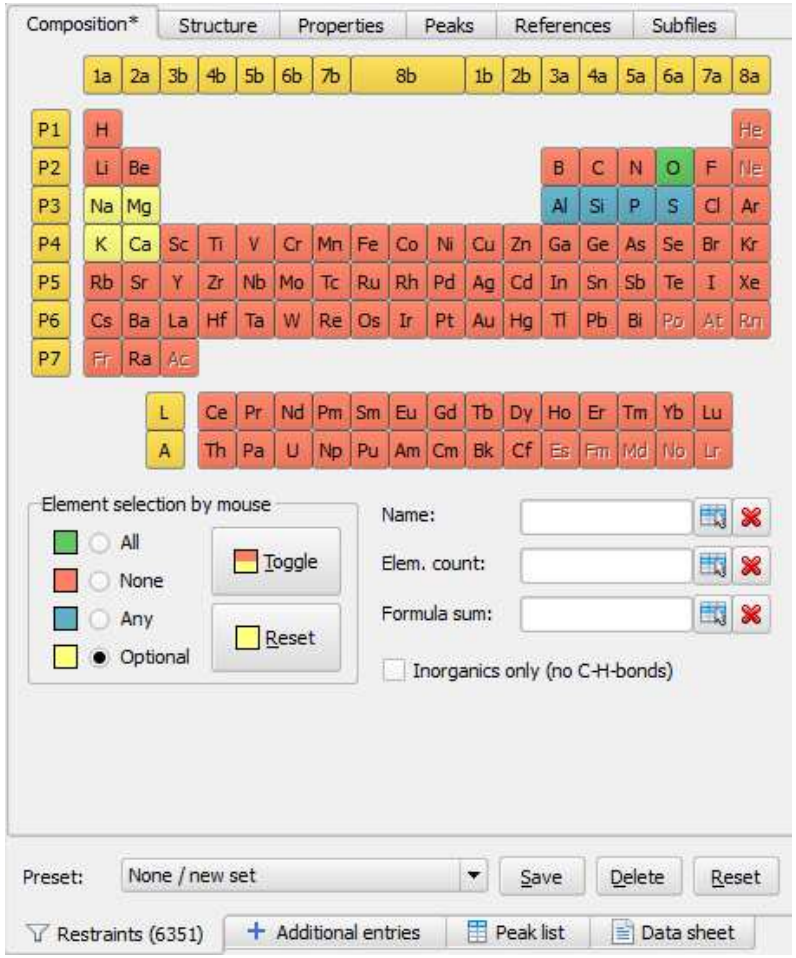
Programme	Publisher	Supported Databases*
HighScore	PANalytical	PDF-2/4 COD
EVA Search/Match	Bruker	PDF-2/4
PDXL2	Rigaku	PDF-2 COD
RayfleX	GE	PDF-2/4
Sleve	ICDD	PDF-2/4
Match!	Crystal Impact	PDF-2/4 COD
CSM	Oxford Cryosystems	PDF-2/4
Jade	MDI	PDF-2/4

+ many more
(see http://www.ccp14.ac.uk/solution/search-match.htm)

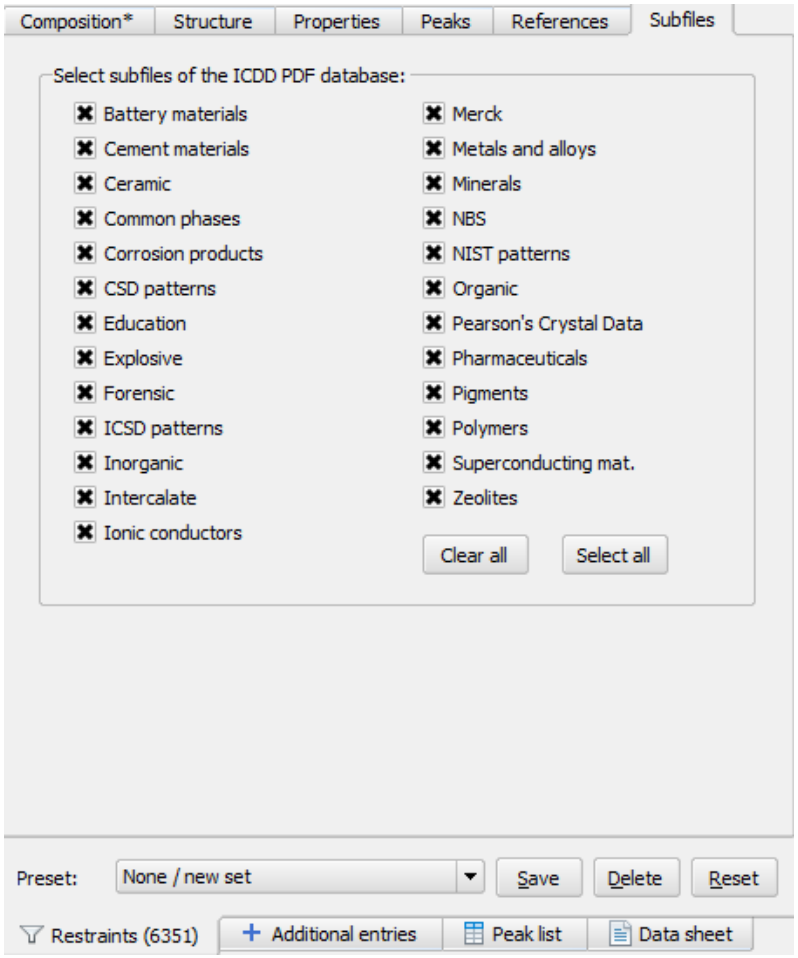
*incomprehensive

Search / Match: Restrictions

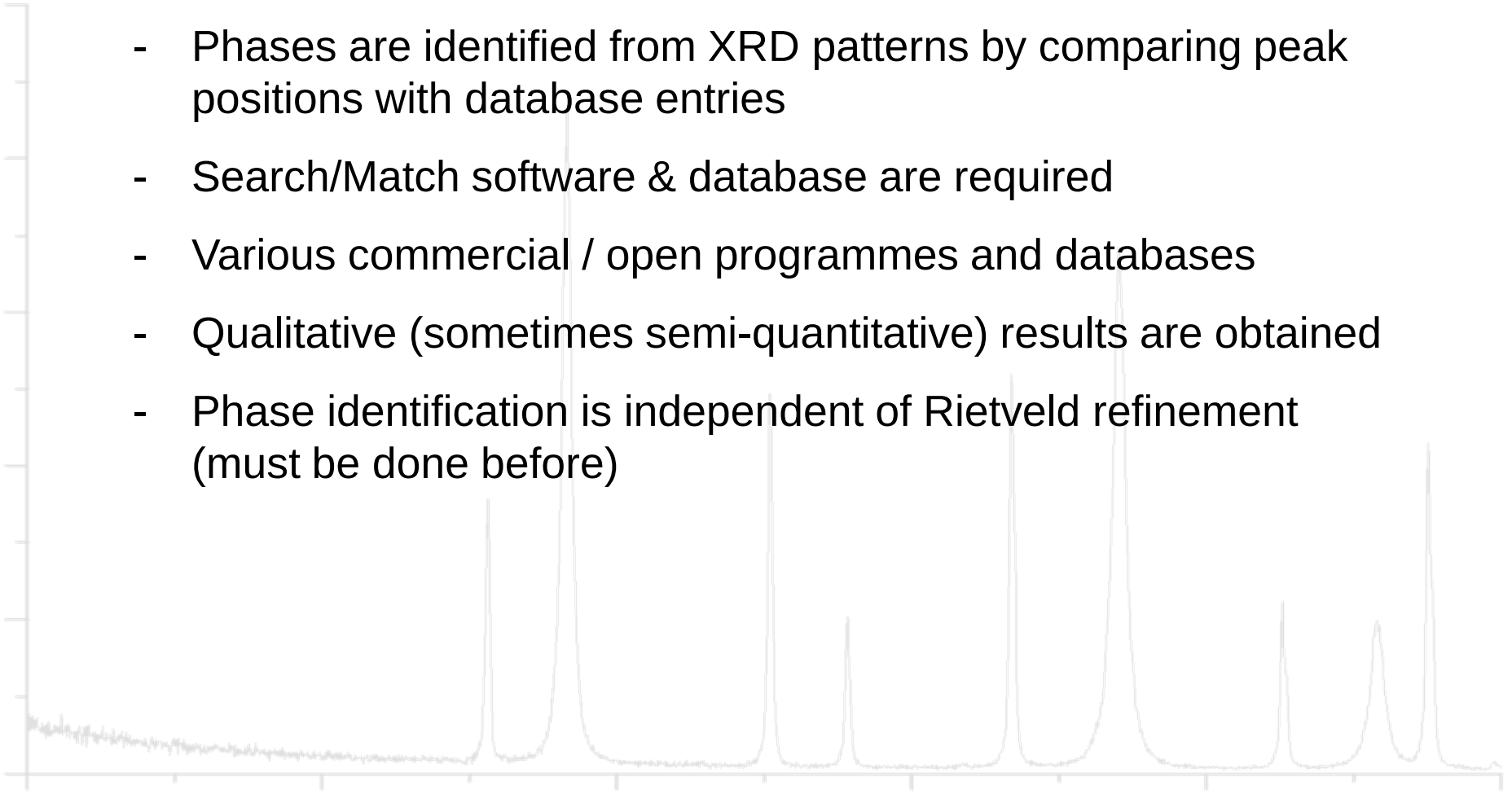
By chemical Composition



By Subfile



Summary: Phase Identification I



- Phases are identified from XRD patterns by comparing peak positions with database entries
- Search/Match software & database are required
- Various commercial / open programmes and databases
- Qualitative (sometimes semi-quantitative) results are obtained
- Phase identification is independent of Rietveld refinement (must be done before)

Question I: Polytypes

Is powder XRD the ideal tool to distinguish and identify the following phases?

Phase	Composition	Space Group
Calcite	$CaCO_3$	R-3c
Magnesite	$MgCO_3$	R-3c
Siderite	$FeCO_3$	R-3c

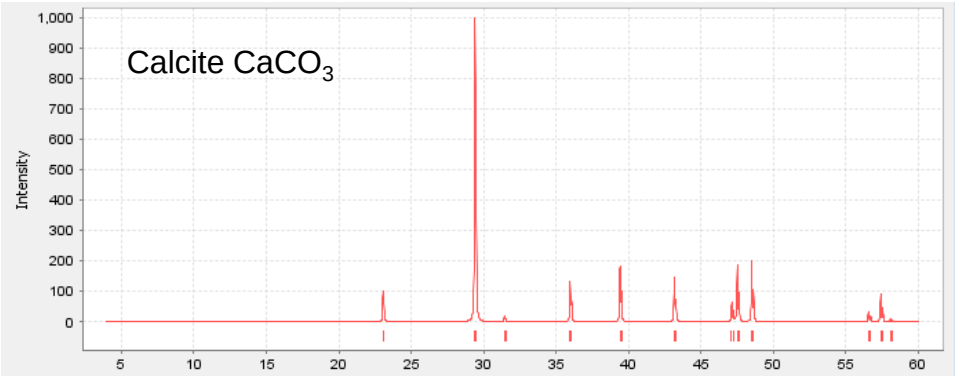
Structurally very similar (polytypes)

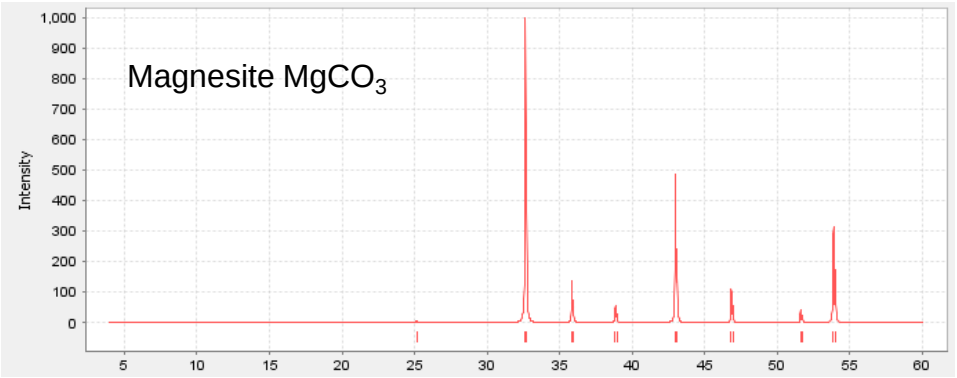
They generate similar diffraction patterns

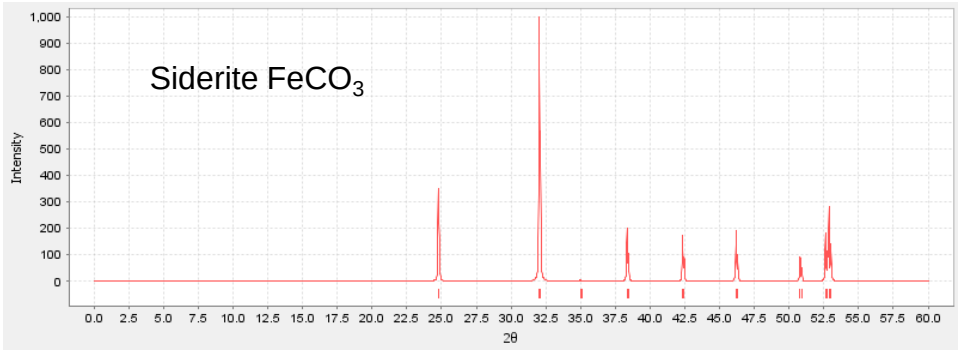
XRD provides no **direct** information on Ca/Mg/Fe content

Only changes in unit cell dimensions.

Question I: Polytypes







- Similar diffraction patterns (mostly peak shifts)
- Some information on Mg/Ca/Fe contens from unit cell dimensions

Solution:
Combine XRD with chemical analysis (ICP, XRF, EDX, XPS…)

Question II: Polymorphs

Is powder XRD the ideal tool to distinguish
and identify the following phases?

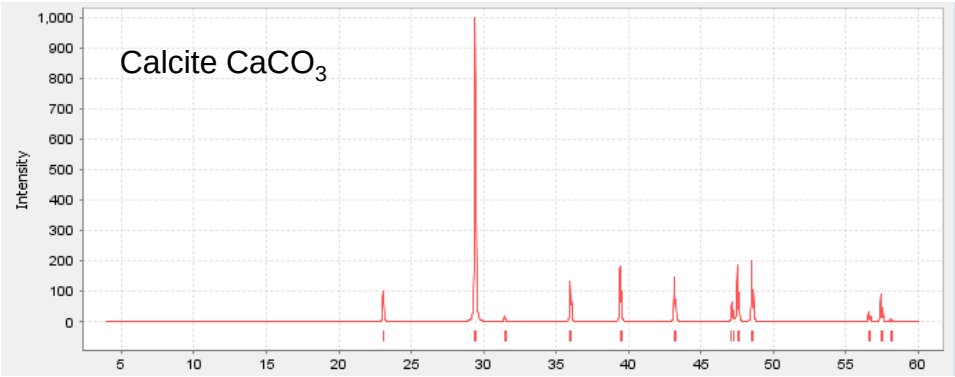
Phase	Composition	Space Group
Calcite	$CaCO_3$	R-3c
Vaterite	$CaCO_3$	P63/mmc
Aragonite	$CaCO_3$	Pnam

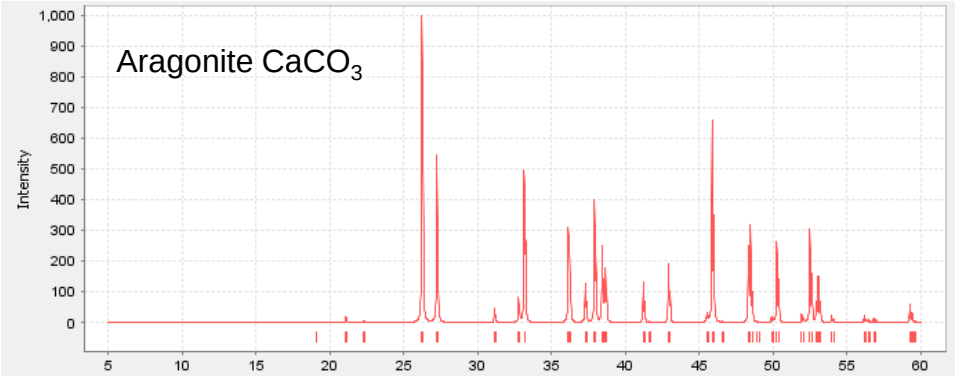
Structurally different (polymorphs)

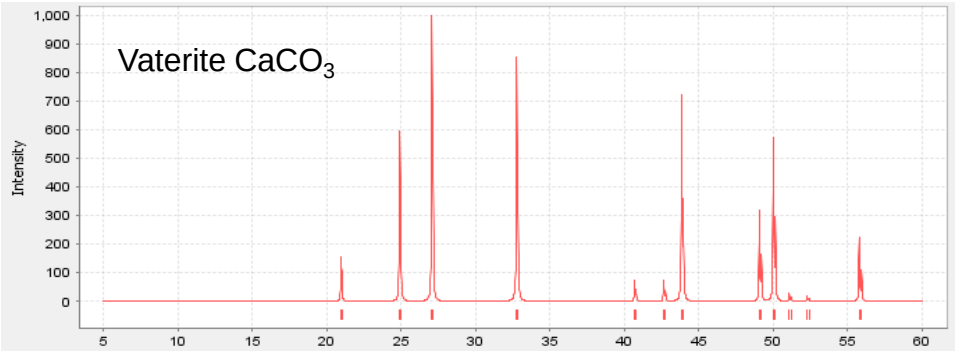
Chemical analyses not able to distinguish (chem. identical)

XRD can easily distinguish

Question II: Polymorphs

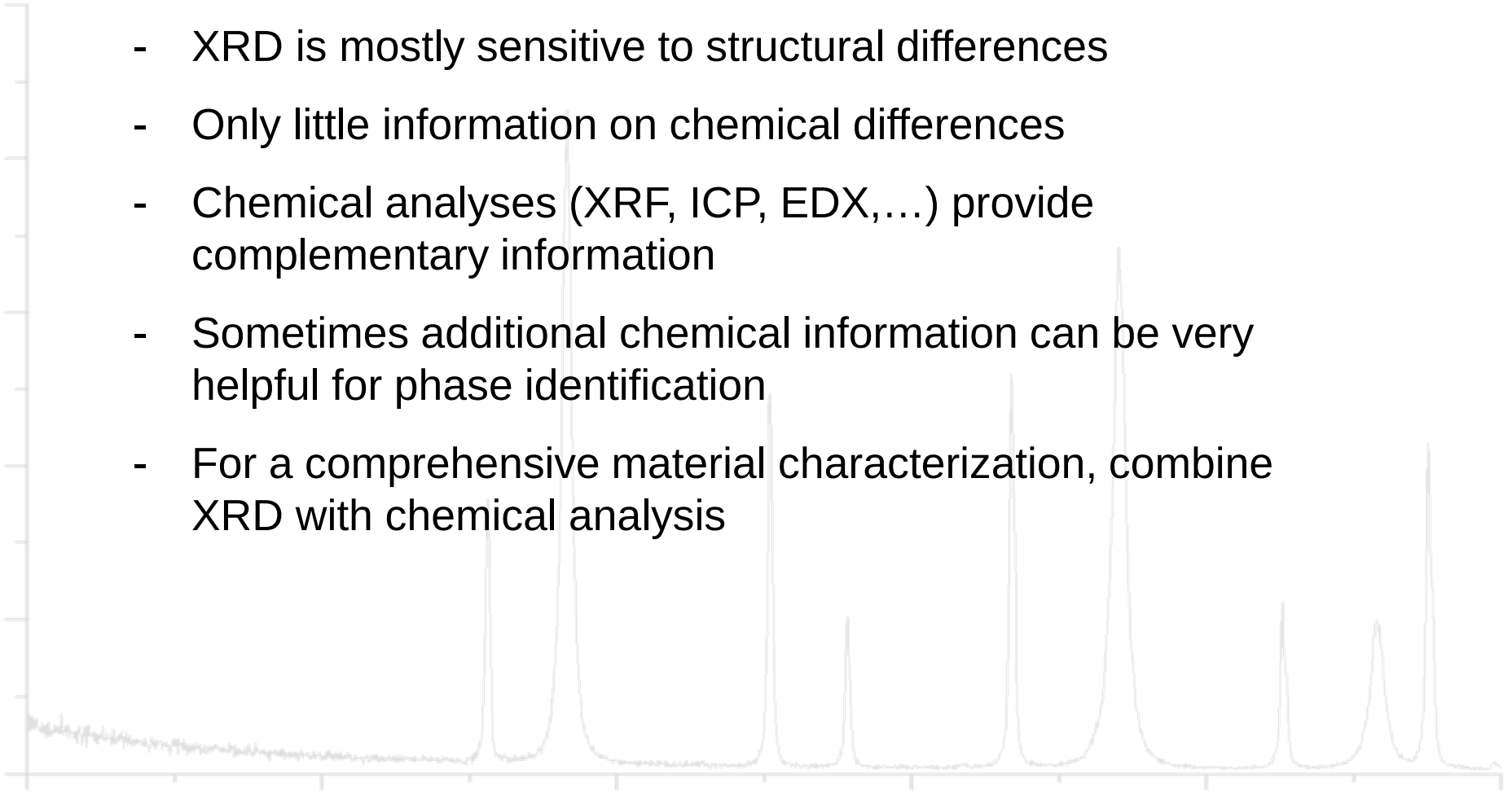






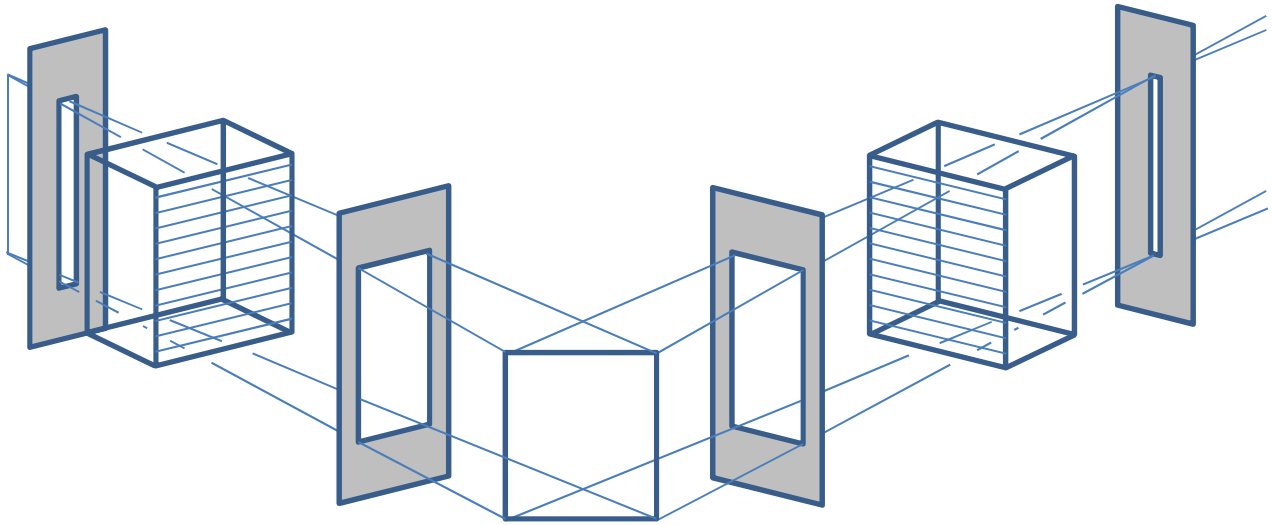
- Strongly different diffraction patterns.
- Easily identified by XRD

Summary: Phase identification II



- XRD is mostly sensitive to structural differences
- Only little information on chemical differences
- Chemical analyses (XRF, ICP, EDX,…) provide complementary information
- Sometimes additional chemical information can be very helpful for phase identification
- For a comprehensive material characterization, combine XRD with chemical analysis

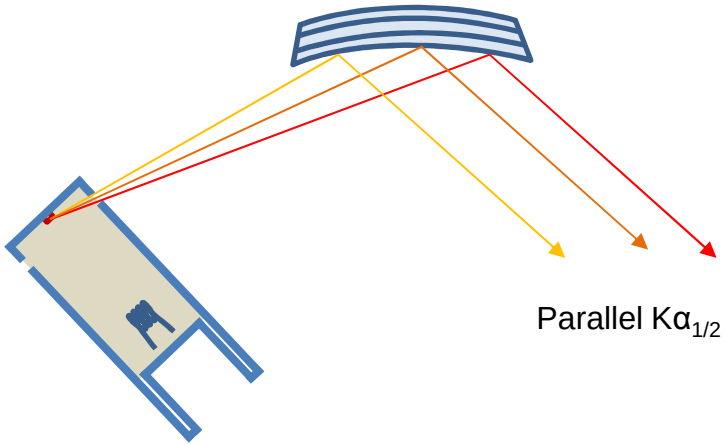
Typical Slit Configuration



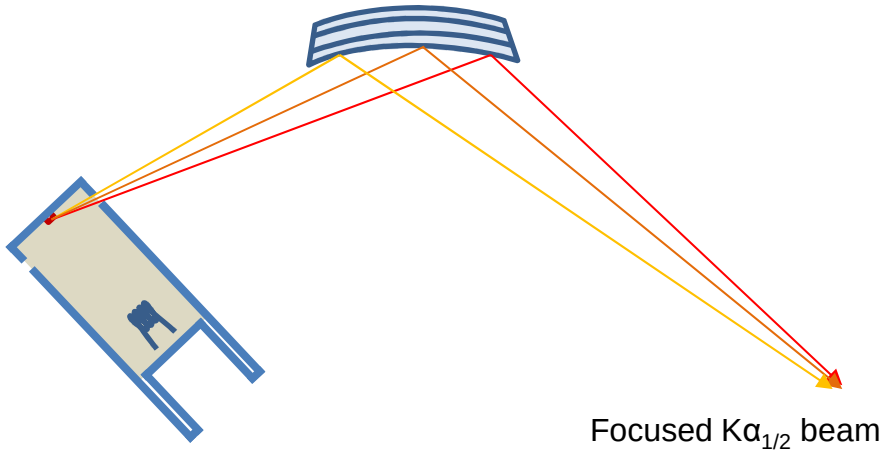
X-ray Mirrors

- Collimators and Divergence Slits cut off intensity
- There are no lenses for X-rays
  (Index of refraction for all materials ~1)
- Bragg diffraction can be used to construct mirrors
- Single crystal with parabolic surface: All beams coming from the tube focus are in diffraction condition for $K\alpha_{1/2}$

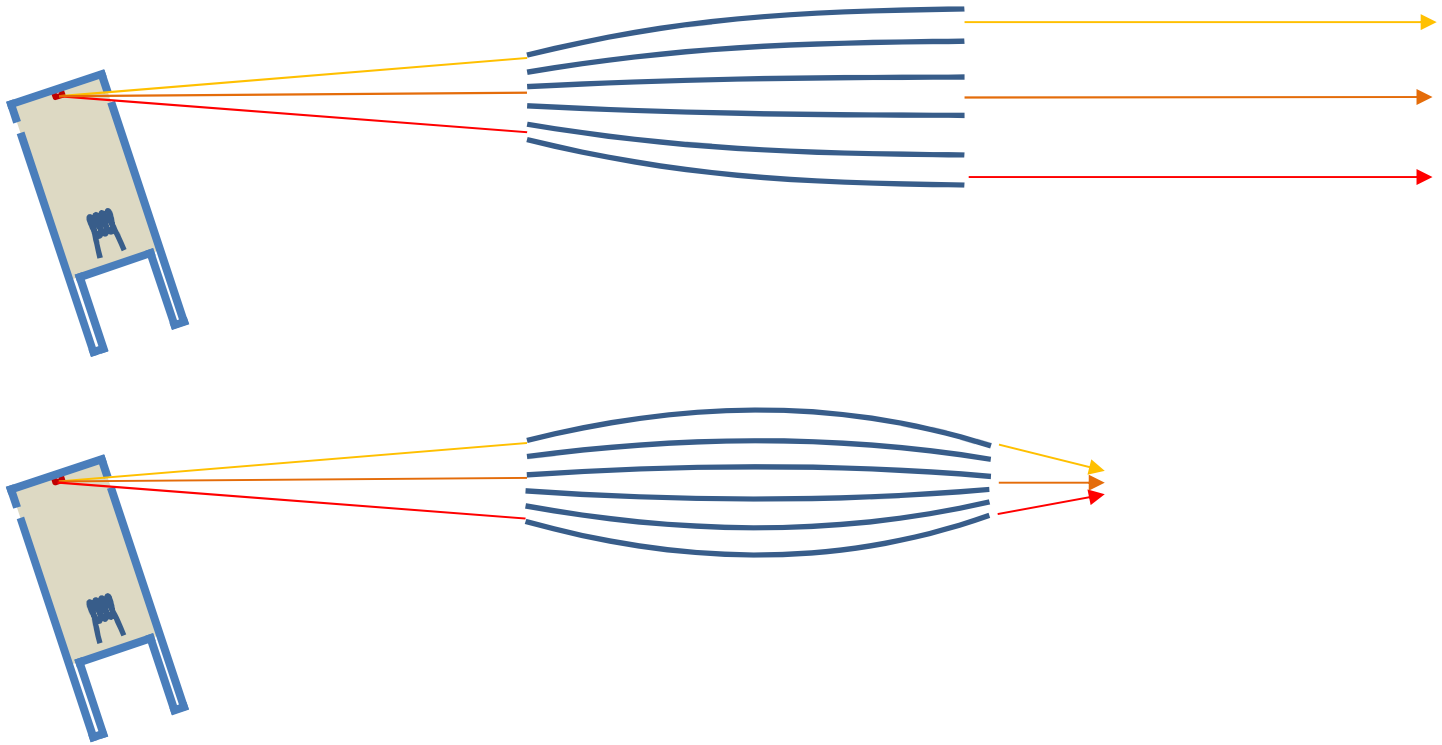
Goebel Mirror



Focusing Mirror



Polycapillary Optics



Latest generation:

Polycapillary glass fiber optics
Conserves most of the primary beam intensity